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THE COMPOSITIONAL STUDY OF NITROGEN AND OXYGEN COMPOUNDS IN PRODUCTS OF HEAVY OIL PRIMARY AND SECONDARY UPGRADING PROCESSES

Final Report

by

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TECHNICAL STAFF CONTRIBUTIONS

Polar components from the products of upgrading processes were preconcentrated by R.N. Yerrow and A. Williams. High performance liquid chromatography separations were carried out by N. Whitelegg. D. Kulawic characterized polar fractions by infrared spectroscopy. Mass spectrometric characterizations were performed by H.P. Fischer and A. Williams. Analytical services were supplied by L.W. Beauchamp and J.E. Coffey. M. Giampuzzi assisted in preparation of the final report. J. Chmielowiec was Project Manager for this program and prepared this manuscript.

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1. SUMMARY

An analytical procedure, which was based on the discrimination of polar compound classes using liquid chromatography followed by mass spectrometric analysis was tested. The chemical intelligence on the fractions obtained from Athabasca bitumen and its upgrading products has been advanced by determining structural characteristics of the nitrogen and oxygen components. This report describes determining the distributions of nitrogen and oxygen compounds in samples from various process streams. This procedure is capable of providing information useful for evaluating hydrodenitrogenation and hydrodeoxygenation reactions.

2. INTRODUCTION

2.1 OBJECTIVE

The primary objective of this program was to characterize nitrogen and oxygen compound types in the upgraded products derived from Athabasca bitumen.

A secondary objective was to evaluate the advantages and limitations of in-house mass spectrometry and infrared spectroscopy methods for analyzing specific classes of polar compounds in naphthas, middle distillates and gas oils.

2.2 JUSTIFICATION

Nitrogen compounds, depending on their nature and concentrations, in charge stocks to catalytic processes (hydro- processes and reforming) can severely limit or poison the catalyst activity. Oxygen compounds are corrosive (especially naphthenic acids) and can promote gum formation as part of the deterioration of the hydrocarbons in the petroleum product.

There is ample evidence that products of upgrading are often more reactive (have a lower resistance to oxidation for instance) than untreated oils. The observed changes in reactivity appear to be related to both the loss of normally occurring inhibitors and the production of new species including nitrogen- and oxygen-compounds. There is no general agreement on the role of specific N- and O-compound types in various charge stocks and products of upgrading. Difficulties exist in identifying molecular structures at low concentrations in process streams. Synergistic effects may also be operating.

An extended insight into the N- and O-components and their levels in products derived from Athabasca bitumen is expected to contribute to improving chemical analyses/characterizations of the synthetic fuels. Providing information on the fate of specific compound types may contribute to more economic processing of synthetic crudes.

2.3 BACKGROUND - LITERATURE REVIEW

Athabasca bitumen contains various organonitrogen- and organo-oxygen-compounds. The primary upgrading based on carbon rejection or hydrogen addition processes significantly reduces the contents of both types of compounds. The elemental nitrogen content may be decreased by several times and new types of nitrogen components may be formed. Susceptibilities of nitrogen compound types to hydrodenitrogenation may also affect their distribution in the upgraded products. There is only limited information available about deoxydation of bitumen, because oxygen is difficult to measure accurately in petroleum streams.

The characterization of the N- and O- constituents is of immediate importance to improve processing synthetic oils produced from Athabasca bitumen. Although the structural characterization of fractions of synthetic oils has received considerable attention, an assessment of the polar species is still a complex problem. Principally, this is because the samples are multifarious molecular mixtures that do not easily lend themselves to direct analysis of any one component or functional group. The related prior literature is reviewed below.

2.3.1 Nitrogen and Oxygen Compounds in Athabasca Bitumen

The papers and reports, which have been published in the seventies, extended insight into the overall composition of Athabasca bitumen. Distributions of elemental nitrogen and oxygen in fractions such as asphaltenes, resins and oils as well as aromatic and polar concentrates have been revealed (1,2). It was found that the bulk of the N- and O- species was contained in the resin and asphaltene fractions. In addition, elemental nitrogen and oxygen contents were observed to increase with increasing aromaticity and polarity of the isolated fractions.

Aiyer et al. have examined the nitrogen components of fractions derived from Athabasca bitumen (3). They concluded that some published values lead to unsatisfactory nitrogen balances caused by isolation problems. The noted discrepancies were explained by

the predominant occurrence of nitrogen and the fact that many of bitumen components contain more than one type of nitrogen atom.

The need for developing correlations between bitumen compositon and the recovery and processing characteristics of Athabasca bitumen has initiated studies on the molecular characterization of the nitrogen- and oxygen-constituents. Polar fractions obtained using API-USBM procedures and their modifications were analyzed for elemental N and O as well as chemical functionalities (4,5). The compound types such as phenols, carbazoles, esters, ketones, amides, sulphoxides and carboxylic acids were tentatively identified.

Moschopedis and Speight carried out acetylations of fractions isolated from Athabasca bitumen (6). Infrared spectroscopic examination of the products indicated that 40-60% of the oxygen present in these materials exists as phenolic hydroxyl groups. In addition, a considerable portion of these groups was concluded to occur as collections of two or more functions on the same aromatic ring or adjacent peripheral sites, or sites adjacent to a carbonyl function in a condensed aromatic system. A more recent study by Moschopedis et al. (7) on nitrogen functional groups in Athabasca bitumen has revealed that the predominant nitrogen groups in resins and asphaltenes exist as imino groups of the carbazole type (7).

A detailed chromatographic study of compound types in Athabasca bitumen asphaltenes by Jacobs and Filby (8) has led to findings consistent with earlier claims of Moschopedis and Speight (9). Namely, while the data did not provide evidence for peripheral nitrogen groups outside the ring structure, the majority of the O atoms occurred in ring substituents.

The upgrading of Athabasca bitumen was found to influence the distributions of polar functionalities. Changes in chemical composition due to deoxygenation and incomplete denitrogenation during thermal hydrocracking included complete decarboxylation and carbazole formation, respectively (10). This observation is consistent with differences in susceptibility to denitrogenation and deoxygenation of polar compounds (11,12). In conclusions, it is expected that various upgrading processes, while aiming at complete denitrogenation and undefined deoxygenation, may lead to

various intermediate polar compounds and selective enrichments of specific functionalities. Therefore, the distribution of N- and O- compounds in heavier products derived from Athabasca bitumen is of particular interest.

2.3.2 Techniques of Analysis of Nitrogen and Oxygen Species

Elemental analysis of heavier fractions for nitrogen is conducted routinely employing the Kjeldahl method, which has been the method of choice in the petroleum industry for many years (13). However, the method is time-consuming, somewhat hazardous because of sample digestion with sulfuric acid, and not too reliable at low concentrations. Therefore, routine nitrogen determinations in lighter fractions are carried out more efficiently by rapid combustion with chemiluminescent detection of nitric oxide (14).

The elemental oxygen contents of petroleum fractions are usually difficult and/or frustrating to carry out for various reasons. The oxygen contents are highly variable and determinations are confused by possible sample oxidation either during crude recovery or sampling of process stream. Suspected air oxidation products are ketones (15,16) and sulphoxides (17). According to the same authors phenols, carboxylic acids and furans are not thought to be major oxidation products. Analyses for elemental oxygen by application of the Unterzaucher combustion technique are often of questionable reliability. Methods employing neutron activation technique or selective conversion to carbon monoxide with infrared detection have advanced considerably the art of the bound oxygen determination, but were not assured high reliability. Finally, one should also be aware that some data reported in the literature were obtained from the difference between the total sample weight and the sum of weights of other determined elements, thus adding more confusion.

Methods of analysis and characterization of tar sand bitumens were reviewed elsewhere (18,19). Many novel, more recent approaches have furthered the compositional analysis for molecular characterization. Prior separation of bitumen into simpler subfractions amenable to structural/compositional characterization or further separation was accepted as a prerequisite for discrete characterization of the polar constituents of bitumen. The scheme

called SARA (for saturates, aromatics, resins and apphaltenes after work of Jewell et al. (20)) was applied for preparing fractions to be investigated for polar components. Another scheme, usually a modification to the API-USBM Project 60 procedure, allowed the isolation of acidic, basic, and neutral nitrogen fractions (4). These fractions were named after the procedure which involved chromatographic separations on anion and cation exchange resins and coordination with ferric chloride, respectively.

Sequential elution schemes have circumvented the major drawback of the API-USBM scheme i.e. transfer of sample from one column to another one. They were reported to yield polar fractions dominated by various functional group types (21-23).

Recently a new concept of discriminating among compound classes such as hydrocarbons, aza-compounds and proton-donating compound types have been proposed (24). Excellent separation of nitrogen heterocyclics from hydroxyl aromatics was achieved (25). Subsequently the compositionsl study reported herein has been undertaken to demonstrate and verify this concept on products derived from Athabasca bitumen.

In addition to the above primary separation procedures, various secondary procedures have been or can be applied for analyzing nitrogen and oxygen compounds. The techniques applied include high performance liquid chromatography (HPLC) (26,27), thin-layer chromatography (TLC) (21), and gas chromatography (GC) (28,29). Due to the abundance of papers on this subject and limited scope of this review, only the most recent papers are cited here.

There are several spectroscopic techniques, which are useful for determining functional nitrogen and oxygen types. Low electron energy high resolution mass spectrometry (HRMS) (30-32), gas chromatography-mass spectrometry (GC/MS) (33,34), infrared spectroscopy (IR) (4,35,36) and nuclear magnetic resonance spectrometry (37,38) provide discrete compositional information. Structural information about the nature of the functional groups may be also derived from non-aqueous potentiometric titrations in the presence of model compounds (39). Such titrations stem from colorimetric and potentiometric titrations used routinely for determining the basic nitrogen content.

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3. EXPERIMENTAL

3.1 SAMPLES

Information on the origin of th studied samples is compiled in Table 1. The samples comprise distillates derived from untreated Athabasca bitumen and its upgrading products. The fractions selected for this study were intended to represent samples of relatively high content of polar species.

TABLE 1 SAMPLES STUDIED

Crude/Fraction	Source	Samples
Athabasca Bitumen Overhead (ABO)	Syncrude Plant Site - Hot Water Process	Middle Distillate (195-360°C) Gas Oil (360-504°C)
Athabasca Bitumen DRB Effluent (ABDE)	Gulf Canada, R&D Dept. Pilot Plant - Donor Refined Bitumen Process (hydrogen addition by means of a donor)	Naphtha (IBP-190°C) Gas Oil (360-504°C)
Syncrude Synthetic Crude Oil (SSCO)	Edmonton-Ft. McMurray pipeline (sample taken Feb. 27/83) - fluid coking followed by hydrotreatment	Middle Distillate (149-385°C) Gas Oil (385°C+)
Syncrude Raw Coker Crude Oil (SRCCO)	Syncrude Plant Gas Oil sample fractionated into 385°C- and 385°C+ cuts in Gulf Canada R&D Dept.	Naphtha (IBP-356°C) Middle Distillate (260-385°C) Gas Oil (385°C+)
Mildly Hydrotreated Syncrude Gas Oil (290°C+) (HTSGO)	Edmonton Refinery. Sample mildly hydrotreated in Gulf Canada R&D Dept.	Gas Oil (360°C+)

3.2 EXTRACTION OF POLAR CONSTITUENTS

The samples with an equal quantity of DMSO containing 6% of water were shaken for 2 h, and left overnight at room temperature to disengage. Then the phases were separated. The extractant was distilled off under vacuum at 160°C from both phases to yield polar extract and raffinate.

3.3 SEPARATION OF POLAR CONSTITUENTS BY LIQUID CHROMATOGRAPHY (LC)

30 g samples were separated on two detachable gravitational flow glass chromatographic columns. The upper column (25 cm x 10 mm I.D.) was packed with clay absorbent (Florex AA-LVM, 250-600 m, Floridin Co.). The lower column (50 cm x 10 mm I.D.) was packed with equal amounts of Silica (Silica Gel, 75-150 m, grade 923, Davison Chemical Div.) and alumina (Alumina F-20, 750-150 μm, Alumina Co. of America). The silica and alumina packings were activated at 220°C for 24 hours and 400°C for 16 hours respectively. The clay was dried at 220°C for 16 hours and hydrated to 12% w/w H_2O.

The saturates were eluted with 70 mL hexane from the combined columns. The aromatics were eluted from the silica/alumina colum with 75 mL diethyl ether followed by 70 mL 80:20 diethyl ether/methanol. The polars were eluted from the clay column with 70 mL 80:20 diethyl ether/methanol. The effluents containing saturates and aromatics were combined. Then, the effluents containing hydrocarbons and polars were left for 24 h in the fumehood to allow eluent vaporization and yielded LC raffinate and LC polar fractions, respectively.

3.4 HPLC FRACTIONATION

The HPLC system (Series 8800) from DuPont (Wilmington, DE) consisting of a gradient controller, pump, UV spectrometer, and column compartment equipped with Rheodyne injection valve was used. Preparative scale separations were performed employing a 250 x 25.4 mm silica (Partsil, 10 μm) column from Whatman, Inc. (Clifton, JN) and solvent system described elsewhere (24). The fractions were collected using fraction collector (Model 201) from Gilson (France). The eluent composition and cut points are shown in Figure 7.

Carbon tetrachloride was used as a solvent for preparing solutions of the extracts and LC polars. The concentrations of the solutions ranged from 100 to 125 mg/mL. The 1 mL samples were injected on the column. Flow rate of 15 mL/min was used in all the separations.

3.5 GC-MS CHARACTERIZATION OF MOLECULAR TYPES

A GC-MS system from Kratos, Manchester, England, consisting of a Carlo-Erba 4160 Gas Chromatograph, a MS-25 low resolution mass spectrometer and a DS-55 Data Acquisition System, were used for the analyses.

The samples were dissolved in a suitable solvent (e.g. Hexane, THF Methanol or Methylene-chloride) and approximately 1 µL of the diluates were injected onto the GC capillary column.

The operating parameters for the instrumentation were as follows:

Gas Chromatograph:

Splitter	20/1 split
Col. Injector	335°C
Temperature Program	80°C initial 4°C/min. ramping 280°C final 280°C isothermal
GC-MS Interface Temp.	280°C
GC-MS Interface	direct heated capillary into MS ion-source
GC Column	30 m x 0.32 mm I.D. cross-linked methyl silicone capillary column
Carrier Gas	Helium

Mass Spectrometer:

MS-25	EI-mode at 57 e.V. nom.
mass-range	m/e 40 - 600
scan speed	approx. 2s/mass decade

The DS-55 datasystem was used to collect, identify, semiquantify and plot the mass spectral data. Specifically, characteristic molecular- and fragment-ions were plotted to obtain semiquantitative group-type information and molecular profiles on a large variety of hetero-atomic component types.

3.6 HRMS DETERMINATION OF MOLECULAR TYPES

The mass spectrometric analyses on selected extracts were performed on an AEI MS-902 high resolution mass spectrometer from Kratos, Manchester, England. The lower boiling samples were introduced through a heated glass batch inlet system at 280°C (1 L expansion volume/molecular leak). The less volatile samples were introduced directly into the ion source by means of a heatable probe (200-300°C at 10^{-7} torr). The mass spectrometer was operated at a dynamic resolution of 10,000 minimum and scans were collected at about 3 minutes per mass decade. The ion source operated at 250°C in the EI-mode at an electron beam energy level of 57 eV nominal.

2-3 µL of sample plus 1 µL of PFK (perfluoro- kerosene internal standard) were introduced through the heated glass inlet system. For the probe analyses only about 0.2 mg of sample were submitted to the mass spectrometer.

Several spectral scans with a constant total ion current and consistent number of peaks were used for the computations and interpretations.

The atomic compositions for all observed mass peaks were computed on a Kratos DS-55 datasystem/DG Nova-3 computer. Possible atomic compositional data for molecules containing up to two heteroatoms from S, O and N were permitted in the computations. Subsequent data reductions and manipulations used special in-house custom software.

The computed compositional possibilities for all observed peaks were reduced to their most likely ones by selecting those atomic compositions with the smallest deviation from the observed masses. The reduced data were subsequently grouped by their Z numbers and the validity of the data was assessed by their abundances and assigned compositions. Thus, frequently observed random peaks with compositional assignments for particularly $C_nH_{2n\pm z}SO$, N_2 and O_2 were often rejected. Further adjustments and reassignments to other hetero group types were necessary because the mass spectral peaks were not always resolved. The intensities of the reduced data were summed by their Z numbers and the group type summations were applied to our in-house 39x39 polar matrix. This matrix is calibrated to resolve the group-type compositions for polar molecules with one N or O atom only. The initial matrix

results and percentage values therefore represent polars with one N or O atom. Other polar molecules with 2 hetero atoms (NO, NS, SO, O_2), as well as residual hydrocarbons and sulfur compounds are not included in the matrix results, nor are they broken down by Z numbers. However, these polar types are semiquantitatively assessed by the chemist/mass spectrometrist, and predominant $C_nH_{2n\pm z}X$, Y types are qualitatively highlighted in the sample reports. Approximate average molecular weights were estimated if the molecular ion envelopes for the various polar group types showed sufficient intensities.

3.7 IR DETERMINATION OF NH, OH AND C=O

C=O Determination

Integrated intensity values were measured for the following compounds in both carbon tetrachloride and dioxane, using a Perkin Elmer 283B IR:

anthracene-9-carboxylic acid
cyclohexane carboxylic acid
nona decanoic acid
1,2,3,6,7,8,11,12 octahydrobenzopyrene-9-one
benzanthracene 7,2 dione

Acid and keto type carbonyls could be quantitated separately and the following integrated intensity values were generated and used in calculating sample CO concentrations:

		Units Integrated Intensity x 10^4
Acid carbonyl C=O	1720 cm^{-1} or higher	1.5
Keto carbonyl C=O	below 1720 cm^{-1}	0.8

L $moles^{-1}$ cm^{-2}

All samples were analyzed in either carbon tetrachloride or dioxane, using 1 cm or 0.194 cm cells respectively. In all analyses, a solvent reference was used and subtracted from the sample IR. Band areas were determined using a PE CDS 2B Application Program.

OH Determination

Samples were dissolved in CCl_4, and using 1.0 cm sample and solvent reference cells, peak absorptivity in the 3610 cm^{-1} region was determined. Since MS analysis indicated predominantly phenolic type OH, calculations were made using Σm = 243 L moles cm^{-1}, which is the average determined molar absorptivity of phenol and 2-naphthol.

NH Determination

Carbazole calibrants were prepared in methylene chloride and carbon tetrachloride and molar absorptivities were determined, using the Perkin Elmer 283B IR. Samples were dissolved in either methylene chloride or carbon tetrachloride, using either 0.1 cm cells or 1.0 cm cells, respectively. A solvent reference was used in all analyses and subtracted from the sample spectrum. Integrated peak access were measured using the PE CDS 2B Application Program. The integrated intensity values for carbazole in methylene chloride was 1.33 $Lgcm^{-1}$ and 1.58 $Lgcm^{-1}$ for carbazole in carbon tetrachloride.

3.8 GC ANALYSIS USING THERMIONIC SPECIFIC DETECTOR (TSD)

The samples were diluted 1:10 in acetone and 1.0 µL volumes were injected onto the Varian 3700 gas chromatograph. The instrument conditions were as follows:

Column:	50 m x 0.2 mm crosslinked methyl silicone (liquid phase 0.5 µm)
Oven Temperature:	Initial: 30°C Rate: 2°C/min Final: 260°C
Carrier Gas:	Nitrogen at 1 mL/min
Injection Port Temperature:	270°C
TSD Temperature:	300°C
TSD Hydrogen Flow:	4.5 mL/min at 26 psig
TSD Air Flow:	175 mL/min
TSD Bias Voltage:	-4.0
TSD Bead Current:	as required to obtain recording at 50% F.S., att = 8 x 10^{-12}, approximately 4.0A

Detector output was integrated and collected by the Perkin Elmer 3200 in-house computer.

3.9 DETERMINATION OF BASIC NITROGEN

50 mL Titration Solvent (31 mL chloroform : 69 mL acetic acid) is measured into a 250 mL Erlenmeyer flask. 6-8 drops of Crystal Violet solution (0.1 g/100 mL acetic acid) are added. The solution is titrated to its end point with standardized 0.02N $HClO_4$ solution (1 mL 60% perchloric acid and 1.5 mL acetic anhydride per litre acetic acid).

A known quantity of sample (2-25 g) is added to the flask and the solution is titrated with 0.02N $HClO_4$ solution to its endpoint.

Basic nitrogen is calculated as:

$$\text{Basic N, ppm} = \frac{14010\ N_1\ V_S}{W_g}$$

where N_1 = normality of $HClO_4$
V_S = mL of $HClO_4$
W_g = grams of sample

3.10 DETERMINATION OF TOTAL SULFUR (ASTM D4249)

Sulfur was determined using the ASTM D4249 procedure.

The sample is placed in an X-ray beam and the resultant excited characteristic X radiation is measured. The sample count is measuredd and compared with counts of previously run calibration standards to obtain the sulfur concentration.

3.11 DETERMINATION OF TOTAL NITROGEN (ASTM D3431)

Total nitrogen was determined using a modified ASTM D3431 procedure where a chemiluminescence detector was used instead of a titration cell to determine the amount of NO_x evolved.

The sample is injected into a stream of hydrogen which flows through a pyrolysis tube packed with a Ni catalyst. The sample is converted to NH_3 and detected by chemiluminescence.

3.12 DETERMINATION OF DENSITY (ASTM D4052)

Density was determined by the ASTM D4052 procedure.

Approximately 0.7 mL of liquid sample is introduced into an oscillation tube. The change in oscillatory frequency, caused by the change in the mass of the tube, is compared with calibration data to determine the density of the sample.

4. RESULTS AND DISCUSSION

4.1 METHODOLOGY DEVELOPMENT

Polar compounds present in naphthas, middle distillates and gas oils derived from Athabasca bitumen and its upgrading products were preconcentrated and characterized using an experimental procedure shown in Figure 1. Prior to structural investigation the untreated samples and their fractions shown in Table 2 were analyzed for elemental sulfur, nitrogen, basic nitrogen and oxygen. The results are compiled in Tables 3 and 4.

The polars obtained by two different preconcentration methods were expected to represent the bulk of polar species occurring in the studied materials. Neither method, however, completely removed the polar components. The sequential liquid chromatographic separation did not yield polar cuts (called here LC polars) with complete recovery. Some polar species were retained on the column. Overall sample losses from 1 to 4 wt.% were observed. There were no material losses for the DMSO and nitromethane extractions. However, the extracts contained more hydrocarbons than the LC polars. In general, liquid chromatography was found to produce more polar concentrates. The corresponding nitrogen enrichments can be seen in Figures 2-4.

The DMSO extraction was found to remove preferentially non-basic nitrogen types from most of the treated samples. Figure 5 reveals such trend for five extracts. The same ratio of the non-basic to basic nitrogen species, represented by slope value of 1, was observed for two extracts. Only the extraction of Syncrude gas oil, abundant in the pyrrolic nitrogen components, did not yield such enrichment. Since DMSO does not interact strongly with basic nitrogen species, the lower ratio might be interpreted by the presence of non-basic and basic nitrogen functionalities within the same molecule.

Linear relationships between initial nitrogen content and that in the raffinate are shown in Figure 6. They indicate that nitrogen compounds were removed in amounts approximately proportional to the initial contents. This was not the case for oxygen compounds. The corresponding enrichments were non-linear. Therefore, the concentrated oxygen compounds seem not to represent satisfactorily the bulk of oxygen species present in the samples of Athabasca bitumen origin.

Elemental Analyses of Crude Fractions and Polar Concentrates

The elemental analyses have revealed the highest contents of sulfur, nitrogen and oxygen in the samples of the coker effluent origin. The lowest oxygen contents were found in the DRB naphtha and fractions of Syncrude synthetic crude oil. The highest ratios of N_{basic}/N_{total} and $N_{nonbasic}/N_{total}$ were observed for samples derived from the DRB process effluent and Syncrude synthetic crude oil, respectively.

The LC polars isolated from SSCO and ABDE had the highest nitrogen content. All the DMSO extracts contained more sulfur than the untreated samples. The increased sulfur content, however, was attributed to residual DMSO or its decomposition products rather than significant enrichment in sulfur due to the extraction. This observation remained unexplained during the course of the study.

Preliminary Inspections of Polar Component Types

Preliminary inspections of polar compounds in the concentrates were performed by means of GC/MS (Table 5), UV spectroscopy (Table 6) gas chromatography with nitrogen-specific detector (Table 7), infrared spectroscopy (Table 8) and HRMS.

The IR spectra provided evidence on the presence of NH and OH components in all the concentrates with the exception of NH components in samples of naphtha. The HRMS indicated a diversity of N and O compounds in the gas oil range and it was necessary to use a heatable probe instead of the heated glass batch inlet, since concentrates were found not to be vaporized completely. The analysis by gas chromatography revealed that nitrogen components occur in upper boiling range of naphthas and middle distillates.

Based on the IR determinations of NH and OH components, several observations have been made. The LC polars derived from the coker and DRB effluent naphthas contained approximately equal amounts of OH components, while NH compounds were not detected. The polars from the overhead of Athabasca bitumen and coker effluent middle distillates had high OH contents. The extracts and LC polars derived from Syncrude synthetic crude oil had highest contents of the NH compounds. There were no OH compounds observed in the concentrates of Syncrude synthetic gas oil origin, while the other concentrates of the same boiling range contained only relatively low amounts.

The preliminary assessment has shown that more efficient separation of hydrocarbons from polar components is a prerequisite of discrete molecular characterization of the latter.

Nitromethane Extracts

GC/MS examination found nitromethane extractions to be ineffective. Because of a relatively high hydrocarbon content of these extracts, it was decided not to proceed with their molecular characterization.

Separation and Characterization of Nitrogen and Oxygen Compound Types

In order to improve characterization of polar components, preparative scale HPLC separations were carried out to remove interfering polycyclic aromatic hydrocarbons (PNA's) and discriminate among classes of polar components. The discrimination based on the extent of complexation of various functional groups with DMSO was employed. The separations into three and four fractions were performed using system consisting of a silica column and carbon tetrachloride containing DMSO (Figures 7 and 8). The collected fractions were characterized using IR spectroscopy (Tables 8-11), GC/MS (Table 12) and HRMS. In addition, fractions collected from 'separation into-four' separations were analyzed for total nitrogen content using chemiluminescence analyzer (Table 13).

Mass Balancing

In order to evaluate the effect of the HPLC fractionation on the functional group analysis, the HPLC fractions were mass balanced with whole samples using the equation as follows:

$$X = \frac{\Sigma(\text{Fractional Yield} \times \text{Content})_i}{\text{Total Content}} \times 100\%$$

where : X - recovery factor
i - HPLC fraction

The obtained mean values of the recovery factors are reported in Table 14. Although good mass balances on the weight basis were achieved, they were not followed by those obtained by means of IR spectroscopy. The IR determinations of NH and OH components were only semiquantitatively correct. Large errors in determination of the $\rangle C{=}O$ content might have been caused by possible oxidation of the stored samples and/or poor spectrum deconvolution capability of the dispersive spectrometer.

HRMS provided useful information on the contents of molecules containing one nitrogen atom, while contents of other molecules might be only assessed for qualitative considerations. Due to the limited number of in-house calibrations with cross-checked samples, the latter data were not processed. However, they were used to the limited extent for tentative identifications whenever additional compositional information permitted.

The GC/MS analyses did not yield acceptable mass balances, because of the strong retention of some constituents of the samples studied. The data obtained, however, found use in the process of identifying of predominant component types.

4.2 DISTRIBUTION OF POLAR COMPOUND CLASSES

The HRMS and GC/MS examination of the concentrates separated into three fractions has revealed presence of hydrocarbons in the initial portion of the HPLC effluent, called here Fraction 1. IR data showed maximum contents of unresolved NH and OH types in Fraction 2. It implied limited discrimination among polar compound classes due to the lower resolution of the compound classes than that achieved for the classes represented by model compounds.

Accordingly, the fractionation appeared to be only good enough for separating residual hydrocarbons from proton donating polar compounds and some enrichment of NH and OH species in Fraction 2.

The separation-into-four fractions based on modified eluent composition, was found to be more effective. The distributions of nitrogen and oxygen contents in the HPLC effluent were more consistent with sample characteristics and better reflected affinities of the sample components towards complexation with DMSO.

Based on the model compound data published elsewhere (Anal. Chem. 55 (1983) 2367), some elution order of hydrocarbons, nitrogen- and oxygen- compounds was expected for the separations performed. These separations were assumed to follow the extent of the complexation between DMSO and the solutes. Thus, the sample components were characterized in three categories related to three major envelopes formed by solutes in the HPLC effluents. These categories, reflecting retention characteristics of the chromatographic system, were as follows:

- Neutral compounds (species noninteracting or weakly interacting with DMSO). These comprised hydrocarbons and species with basic nitrogen-, keto-, ether-, -SH, -CN, thioether-, sulfide- or secondary amine-functional group. Fraction 1 was expected to be the envelope of the above solutes.

- Weak proton donors. The compounds with single pyrrolic- or single -OH fall into this category of components retained stronger than neutral compounds. The functionalities, mentioned in the first category, may also occur as secondary contributors to the solute retention. Fraction 2 (for separation-into-three) and Fraction 2 or 3 (for separation-into-four) were expected to contain such compounds.

- Strong proton donors. The compounds present in Fraction 3 (for separation-into-three) and Fraction 4 (for separation-into-four) were expected to comprise acids and polyfunctional compounds. Such compounds were retained stronger than weak proton donors.

Distributions of nitrogen- and oxygen- compound classes in the HPLC effluent are shown in Figure 9 and 10, respectively.

The percent of total content of specific component, P, defined as:

$$P = \frac{\text{Fractional Yield x Content in the HPLC Fraction}}{\Sigma(\text{Fractional Yield x Content in the HPLC Fraction})_i} \times 100\%$$

where: i - HPLC fraction

is plotted against HPLC fraction number.

The distributions of NH types and total N matched each other for three samples derived from Syncrude synthetic crude oil. They were 9 LCP, 10 DHE and 8 LCP. This was expected from the elemental analyses indicating predominantly nonbasic nitrogen species, confirmed later as pyrrolic compounds. Gas oil polars from Athabasca bitumen overhead (1 LCP) and the DRB process effluent did not contain pyrrolic compounds in Fraction 1. High nitrogen contents of this fraction indicated predominantly basic components, while NH containing compounds were abundant in Fraction 2 and 3. In general, the distribution patterns observed for the contents determined by IR spectroscopy (NH, OH and C=O), chemiluminescence (total N) and HRMS (Z numbers) indicated a relationship between resolved solutes and retention characteristics of the solute classes. Such pattern similarity permitted assigning specific Z numbers to predominant components containing nitrogen- or oxygen- functionality.

The structural characterization of the predominant components, in terms of Z numbers, was possible only for a limited number of samples. The complete mass spectrometric analysis of all the concentrates, however, was beyond the timeframe of this program. Next figures show what kind of information one could generate using HPLC followed by IR spectroscopy, total nitrogen determination and HRMS.

Two Syncrude synthetic gas oils samples were investigated in more detail. Their low sulfur and oxygen contents allowed more accurate assignment of Z numbers to nitrogen components than to those of the other concentrates. Figure 11 provides a comparison of nitrogen compounds present in the raw- (9 LCP) and hydrotreated- (10 DHE) gas oils. Higher levels of -15N and -17N Z number compound types were observed for the hydrotreated sample in Fraction 1 and 2. In contrast, Fraction 3 of the raw sample

contained more nitrogen compounds. The Fraction 4 of both samples had low nitrogen contents. In addition, a shift from dominant -19N Z compound types to -15N Z molecules was seen for the hydrotreated sample. The observed abundance of the nitrogen components in different fractions seemed to correspond to the retention characteristics of the predominant components. It was apparent the hydrotreated sample contained nitrogen compounds interacting with DMSO to a lesser extent. Based on the model compound data (Anal. Chem. 55 (1983) 2367), the corresponding enrichments of the nitrogen in Fraction 1 and 2 and the differences in Fraction 4 composition may be explained by the predominance of sterically hindered pyrrolic compounds.

Figure 11 also shows nitrogen distribution in the polars of the DRB process origin. The HRMS data for this sample were less accurate than for Syncrude materials. However, they were plotted for comparison purposes. Higher sulfur content of this sample, than those of Syncrude synthetic crude oil origin, might have affected accuracy of the HRMS analysis. Nevertheless, this analysis was presumably better than that of 1 LCP, since there was no enrichment of the oxygen compounds observed by neutron activation analysis. Marked differences between 9 LCP and 7 LCP samples were seen for Fraction 1 and 4. These differences reflected the presence of basic nitrogen components in the former fraction and higher NH content of the proton donating components of the latter fraction of 7 LCP.

The distribution patterns obtained by means of IR spectroscopy for oxygen compounds such as -OH and C=O component types matched only the mass spectrometric patterns of two samples (see Figure 10). They were 2 DHE and 4 LPC. Relatively high contents of oxygen species in Fraction 4 of four samples were observed by HRMS. These contents attributed to the presence of strong proton-donors, such as acids or polyfunctional species, provided evidence that separation/discrimination for neutral, weak proton-donors and strong-proton donors has been accomplished.

The HRMS and GC/MS data, obtained for polar constituents of naphtha and middle distillate, allowed positive identifications of predominant components for several fractions. These identifications are shown in Table 15. Only tentative identifications were obtained for polar constituents of gas oils.

4.3 COMPARISON OF COMPOSITIONAL CHARACTERIZATION METHODS

A summary of the resulting information has not been complete without assessing the quality and limitations of the generated data, i.e. specific comparison of the used methods for determining types and approximate abundances of polar compounds in naphthas, middle distillates and gas oils.

Three techniques contributed to the characterization to a small extent. These techniques and information obtained were as follows:

- gas chromatography - relationship between nitrogen content and boiling point range
- GC/MS - tentative identification of predominant components
- UV spectroscopy - aromaticity characterization.

The first two techniques provided limited insight into polar material composition due to their applicability only to lower boiling samples. The third technique, more suitable for relative comparisons of samples showing minor differences, was of limited use, since samples were diversified in nature.

Most of the data have been obtained by means of IR spectroscopy and HRMS. The former technique showed to be less effective - the material balance for all compound classes determined by IR methods was not so good as that determined by HRMS. It was apparent that both the calibration curves and deconvolution of spectra were major error sources for the former technique. In particular, the determination of the OH content was adversely influenced by low absorbances observed using the dispersive IR spectrometer. The data obtained employing HRMS were more consistent, although far from being quantitatively correct. These data could be significantly improved by generating more detailed calibrations, i.e. by developing calibrations based on cross-checked concentrates and blends of polar compounds of diversified origin.

In general, elemental determinations and molecular characteristics appear to be in overall agreement, the latter providing more information. The developed separation procedure followed by functional group analysis of the HPLC fractions was found to be capable of providing more discrete characterization of polar components than the direct analysis of polar concentrates.

5. CONCLUSIONS AND RECOMMENDATIONS

The discrimination among nitrogen and oxygen compound classes, by means of liquid chromatography followed by mass spectrometric analysis provides a capability of advancing molecular characterization of process streams for polar components. The results of this project demonstrate the potential for obtaining information on hydrodenitrogenation and hydrodeoxygenation of various process streams.

Future work should concentrate on:

- improving HRMS calibrations, because amounts determined are only semiquantitative;
- investigating HPLC cuts by means of Fourier Transform Infrared Spectroscopy and nuclear magnetic resonance spectroscopy to improve functional group determinations;
- developing algorithms for complete functional analysis of polar compound classes by combination of chromatography and one of the spectroscopic techniques.

6. ACKNOWLEDGEMENTS

The author wishes to thank Dr. I.P. Fisher for many helpful discussions and Messrs. N. Whitelegg, D. Kulawic and P. Fischer for their excellent technical assistance.

FIGURES

Fig. 1 Procedure for the separation and characterization of polar component types

Figs. 2-4 Distributions of nitrogen between concentrate and raffinate

Fig. 5 Ratio N_{basic}/N_{total} in the untreated sample vs. that in extract

Fig. 6 Initial N or O content vs. corresponding raffinate contents

Fig. 7 Calibration of HPLC system. Separation:
A. into three fractions. Standards:
1) anthracene, 2) coronene, 3) acridine,
4) carbazole, 5) naphthol and anthracene-9-carboxylic acid. Sample injected contained appr. 0.5 mg of each compound. Eluent composition was CCl_4/DMSO:
(99.97:0.03) 0 min, (99:1) 0-15 min, gradient-exponent 5 (99:1 to 50:50) 15-20 min, (50:50) 20-35 min.

B. into four fractions. Standards:
1) anthracene, 2) acridine, 3) carbazole,
4) naphthol and anthracene-9-carboxylic acid. Sample injected contained appr. 0.5 mg of each compound. Eluent composition was CCl_4/DMSO: (99.97:0.03)
0 min, (99:1) 0-23 min, gradient-exponent 5 (99:1 to 50:50) 23-24 min, (50:50) 24-44 min.

Fig. 8 Preparative scale HPLC separation of 7 DHE.
Injected sample size: 100 mg
A. Separation into three fractions
B. Separation into four fractions

Fig. 9 Distribution of Nitrogen in HPLC Fractions

Fig. 10 Distribution of Oxygen in HPLC Fractions.

Fig. 11 Distribution of N Z Number Compound Types in the HPLC effluent.

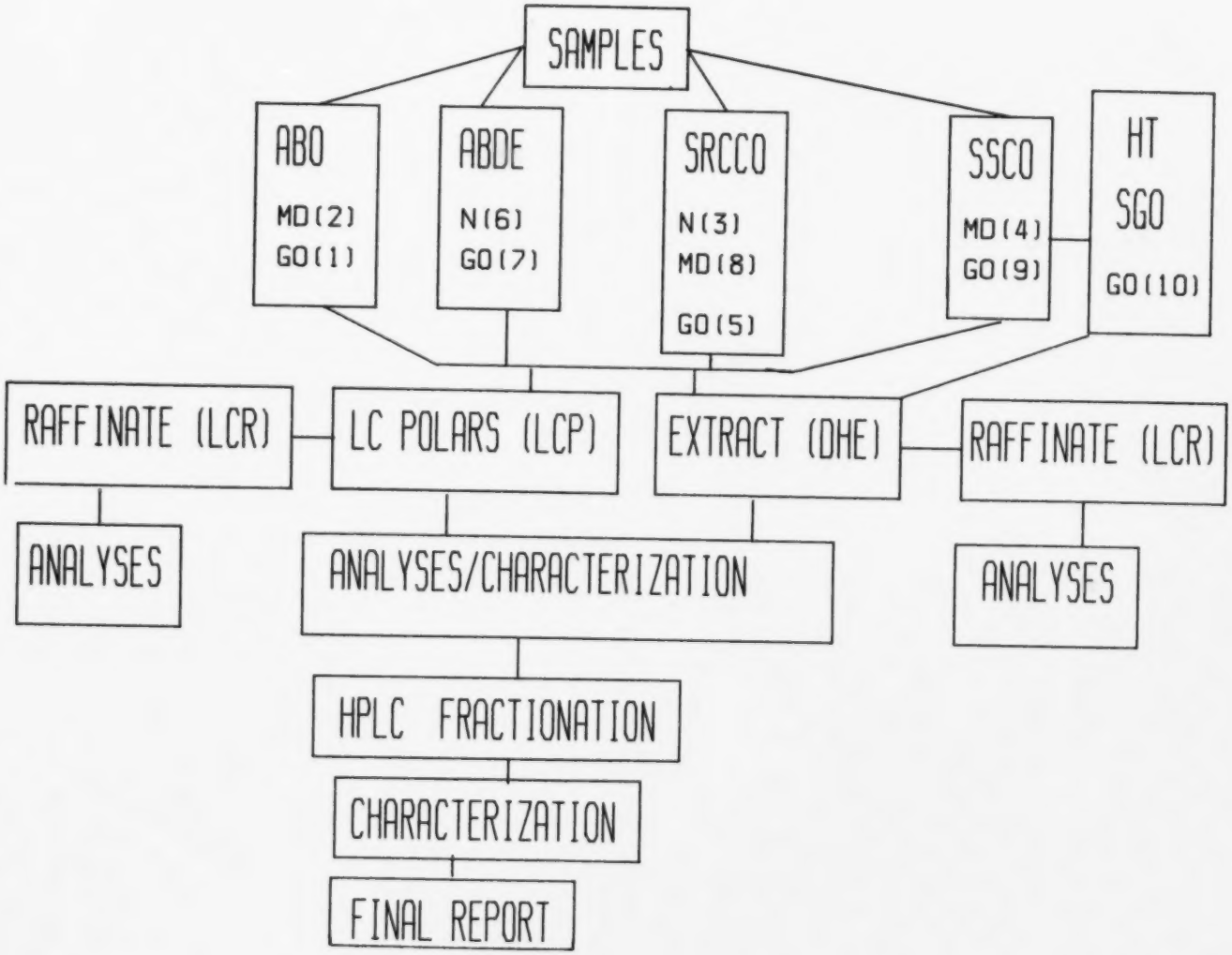
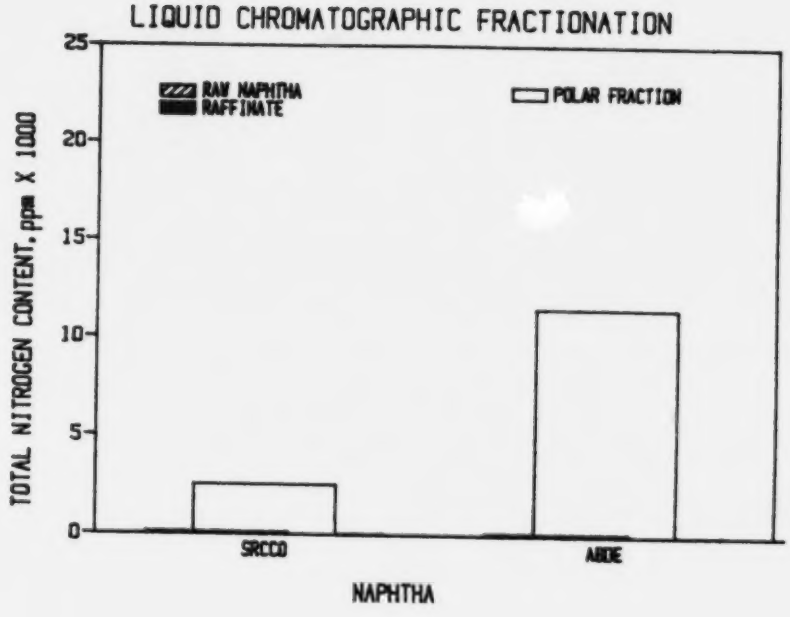

SAMPLES
ABO
MD(2)
GO(1)
ABDE
N(6)
GO(7)
SRCCO
N(3)
MD(8)
GO(5)
SSCO
MD(4)
GO(9)
HT
SGO
GO(10)
RAFFINATE (LCR)
LC POLARS (LCP)
EXTRACT (DHE)
RAFFINATE (LCR)
ANALYSES
ANALYSES/CHARACTERIZATION
ANALYSES
HPLC FRACTIONATION
CHARACTERIZATION
FINAL REPORT

Fig. 1


LIQUID CHROMATOGRAPHIC FRACTIONATION
RAW NAPHTHA
RAFFINATE
POLAR FRACTION
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
ABDE
NAPHTHA

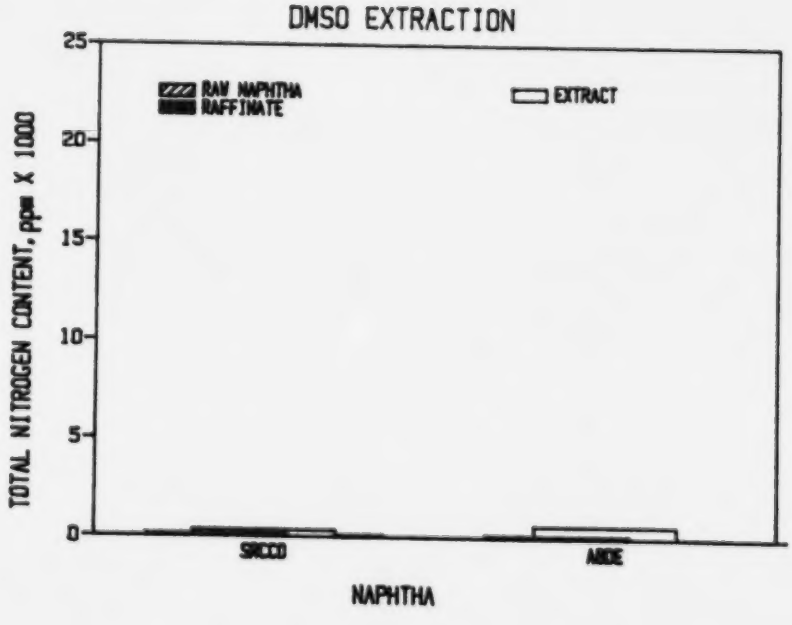
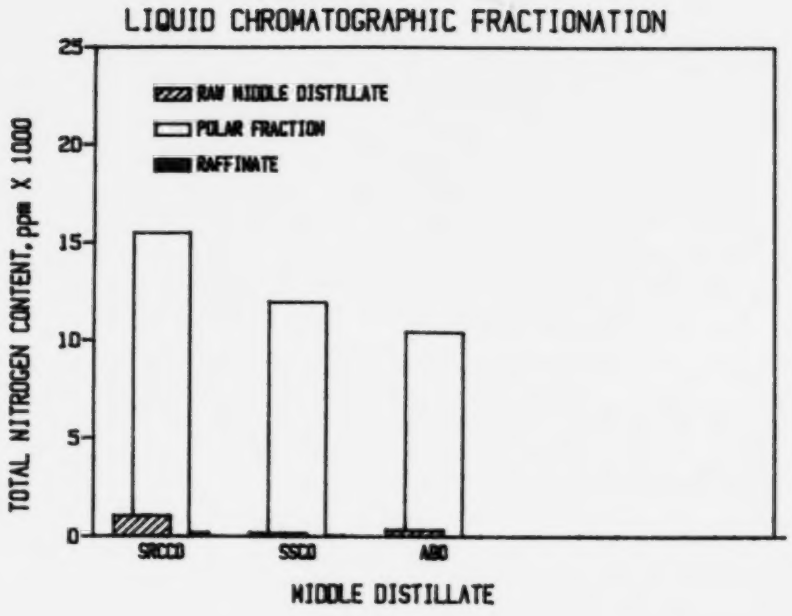

DMSO EXTRACTION
RAW NAPHTHA
RAFFINATE
EXTRACT
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
ABDE
NAPHTHA

Fig. 2


LIQUID CHROMATOGRAPHIC FRACTIONATION
RAW MIDDLE DISTILLATE
POLAR FRACTION
RAFFINATE
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
SSCO
ABO
MIDDLE DISTILLATE

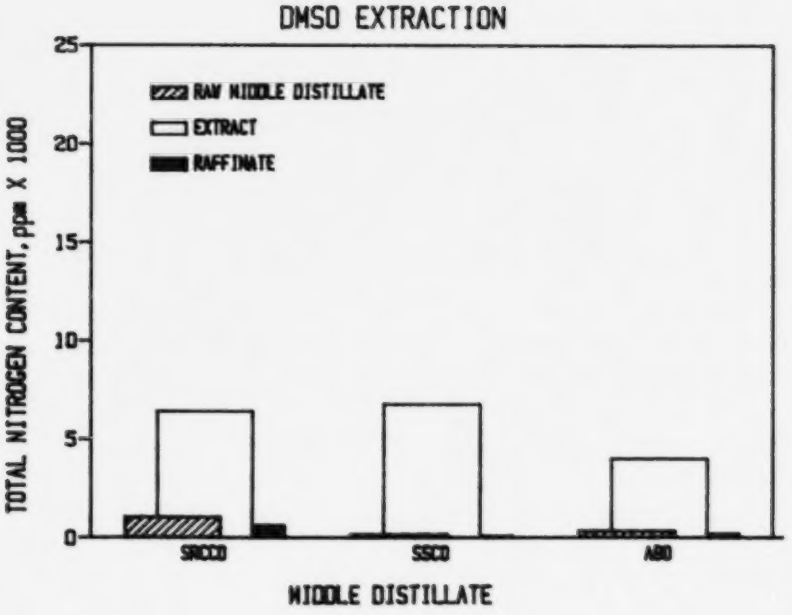
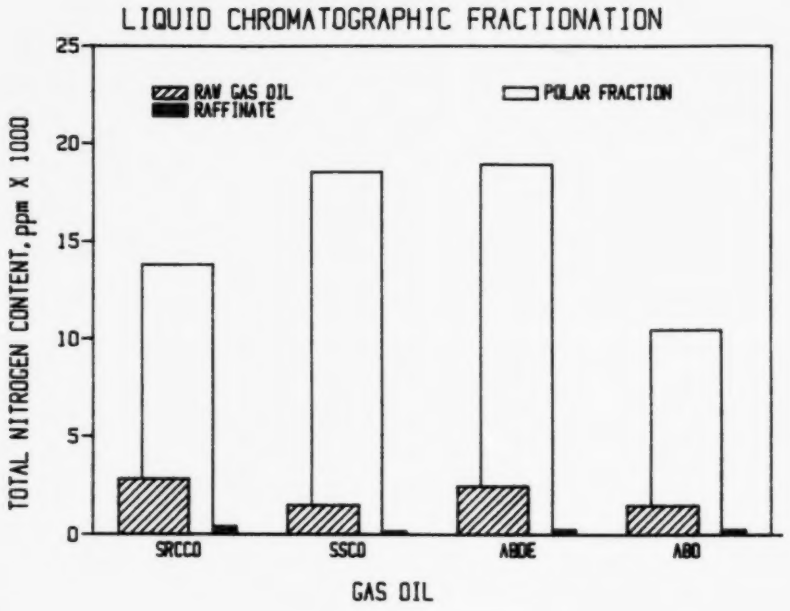

DMSO EXTRACTION
RAW MIDDLE DISTILLATE
EXTRACT
RAFFINATE
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
SSCO
ABO
MIDDLE DISTILLATE

Fig. 3


LIQUID CHROMATOGRAPHIC FRACTIONATION
RAW GAS OIL
RAFFINATE
POLAR FRACTION
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
SSCO
ABDE
ABO
GAS OIL

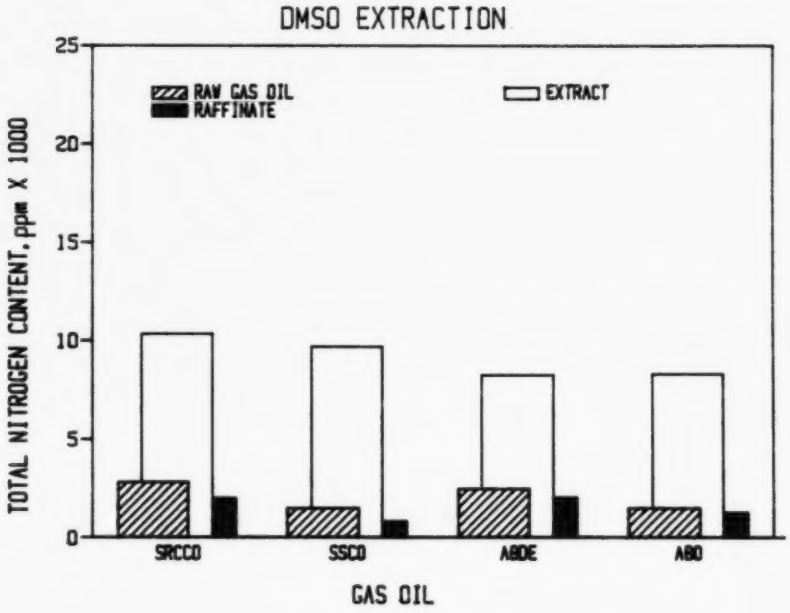

DMSO EXTRACTION
RAW GAS OIL
RAFFINATE
EXTRACT
TOTAL NITROGEN CONTENT, ppm X 1000
25
20
15
10
5
0
SRCCO
SSCO
ABDE
ABO
GAS OIL

Fig. 4

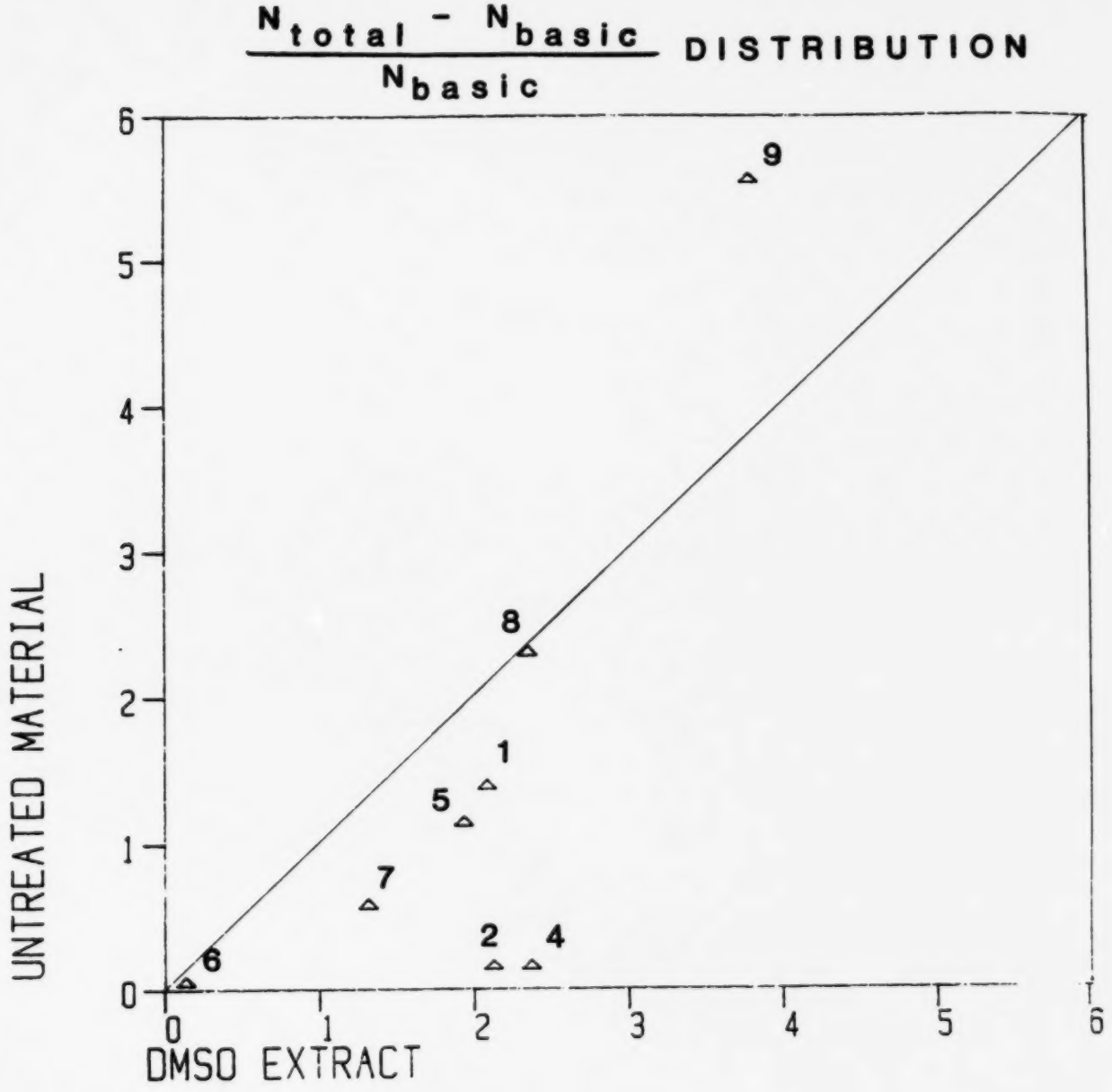

$\frac{N_{total} - N_{basic}}{N_{basic}}$ DISTRIBUTION
UNTREATED MATERIAL
DMSO EXTRACT
0
1
2
3
4
5
6
9
8
1
5
7
2
4
6

Fig. 5

PRECONCENTRATION OF NITROGEN AND OXYGEN COMPONENTS

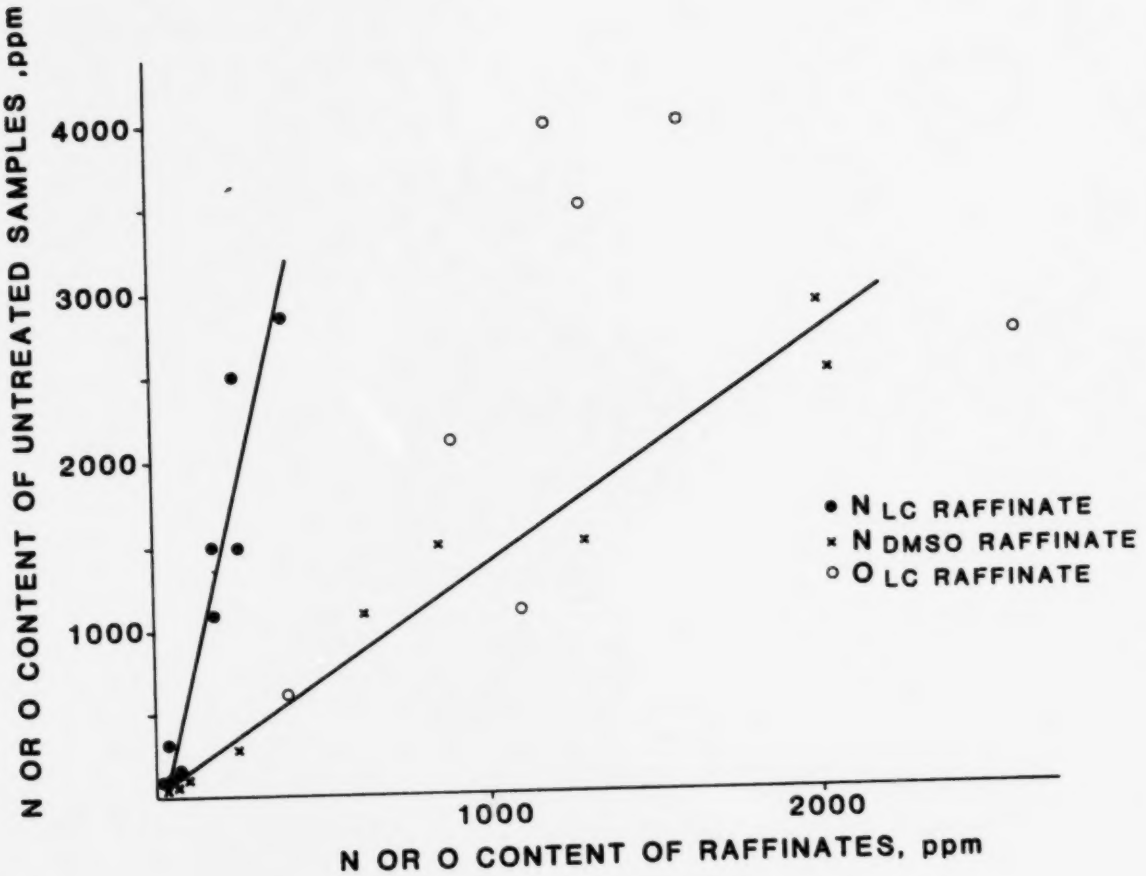


Fig. 6

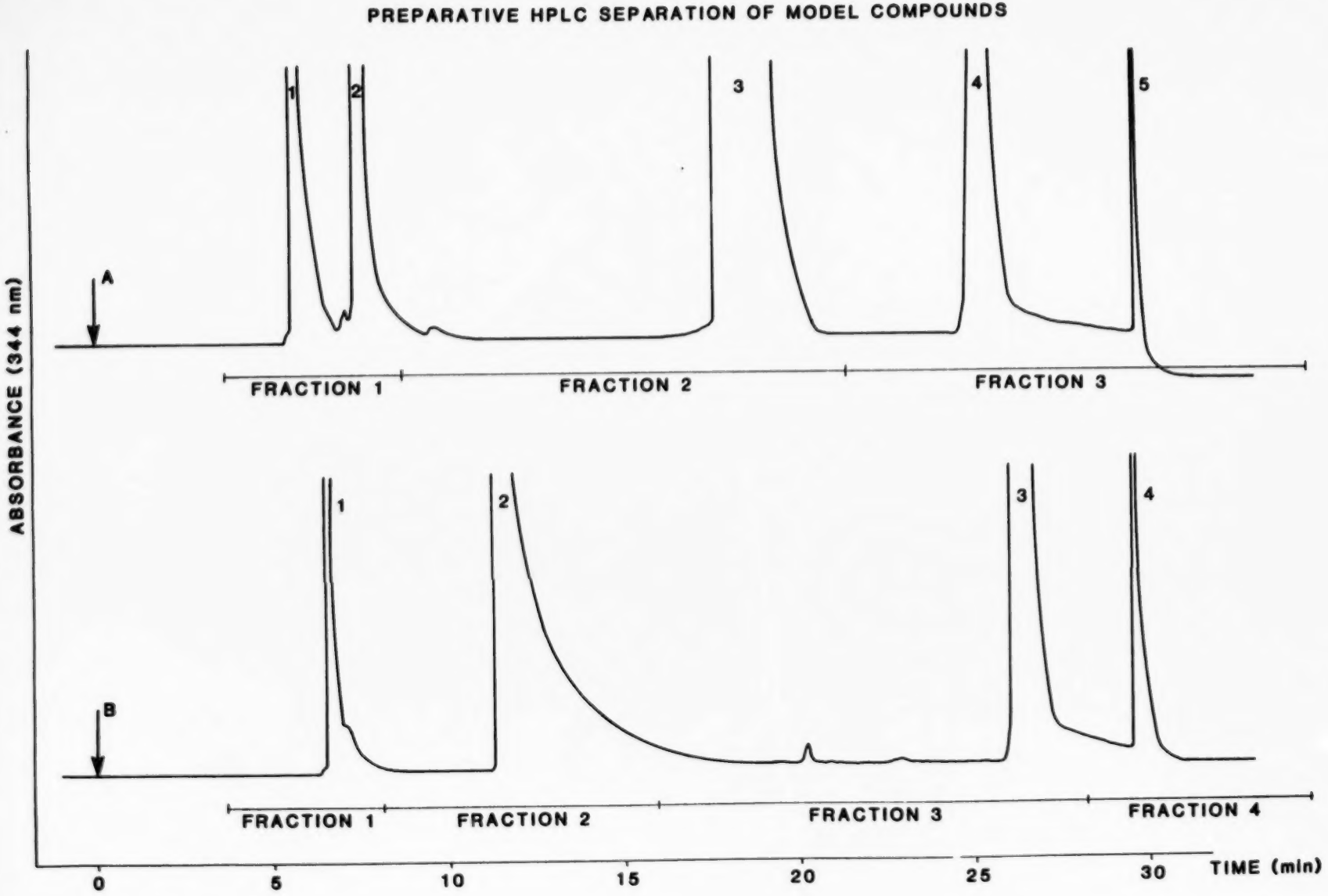

PREPARATIVE HPLC SEPARATION OF MODEL COMPOUNDS
ABSORBANCE (344 nm)
A
1
2
3
4
5
FRACTION 1
FRACTION 2
FRACTION 3
B
1
2
3
4
FRACTION 1
FRACTION 2
FRACTION 3
FRACTION 4
0
5
10
15
20
25
30
TIME (min)

Fig. 7

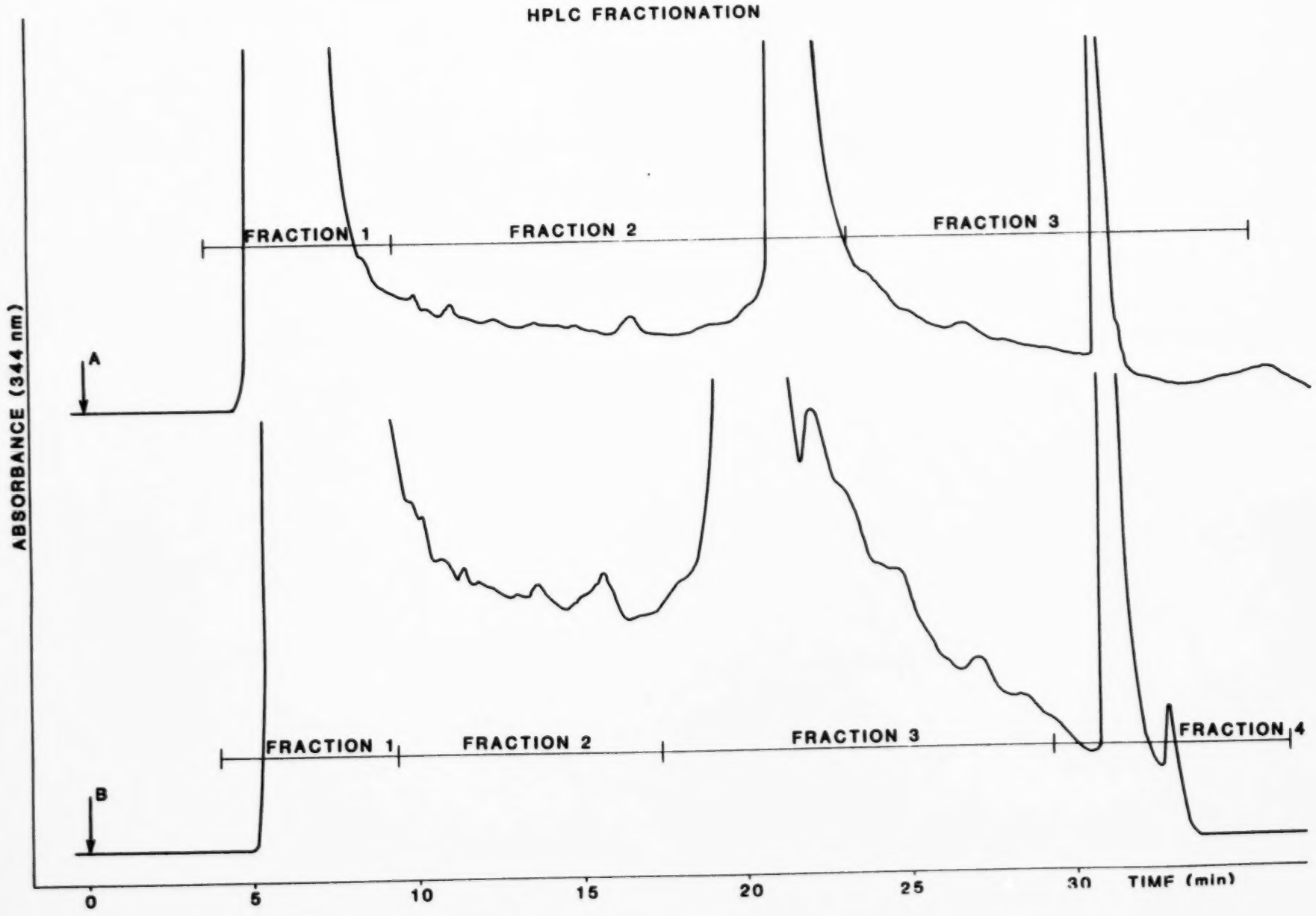

HPLC FRACTIONATION
ABSORBANCE (344 nm)
A
FRACTION 1
FRACTION 2
FRACTION 3
B
FRACTION 1
FRACTION 2
FRACTION 3
FRACTION 4
0
5
10
15
20
25
30
TIME (min)

Fig. 8

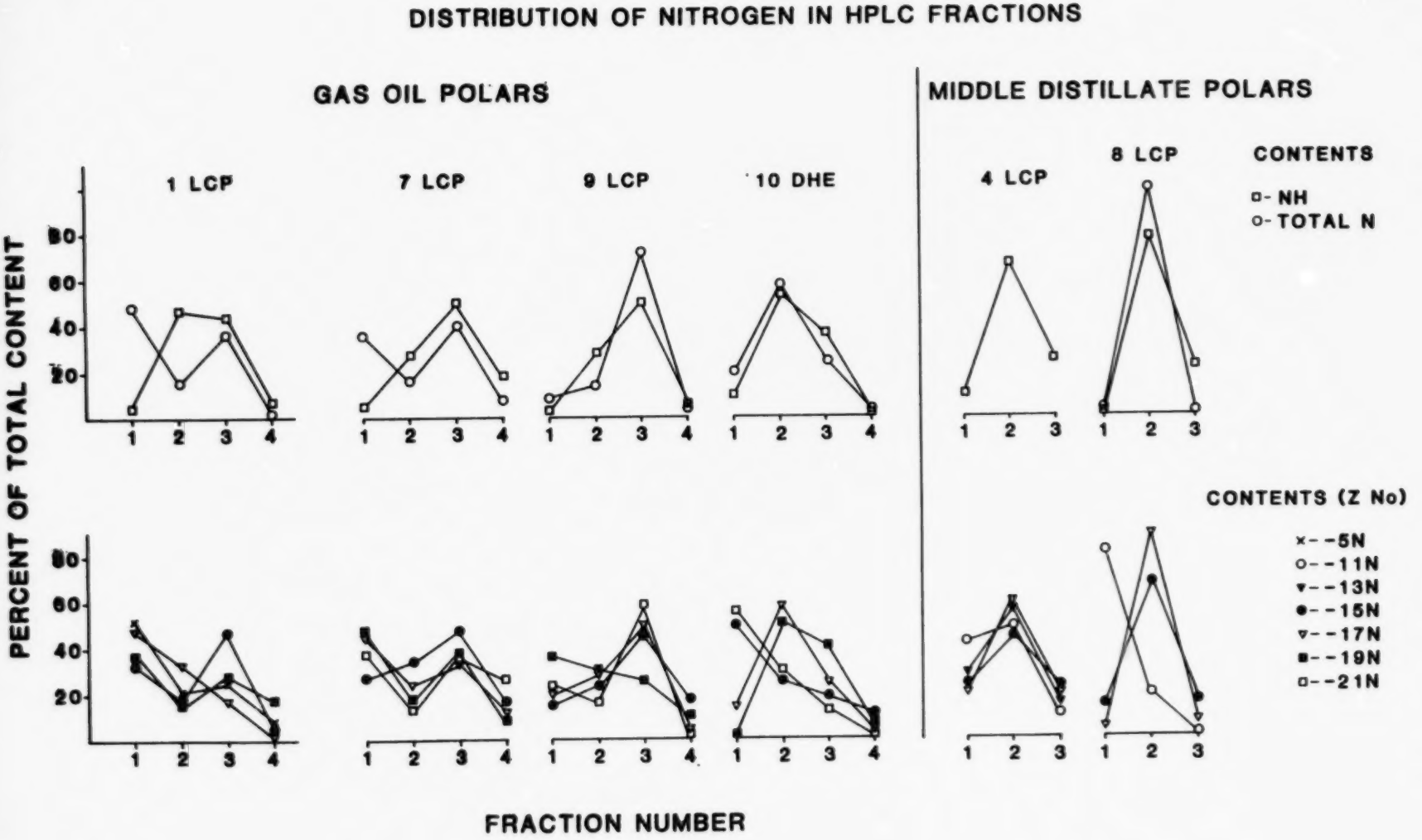

DISTRIBUTION OF NITROGEN IN HPLC FRACTIONS
GAS OIL POLARS
MIDDLE DISTILLATE POLARS
1 LCP
7 LCP
9 LCP
10 DHE
4 LCP
8 LCP
CONTENTS
NH
TOTAL N
CONTENTS (Z No)
5N
11N
13N
15N
17N
19N
21N
PERCENT OF TOTAL CONTENT
FRACTION NUMBER

Fig. 9

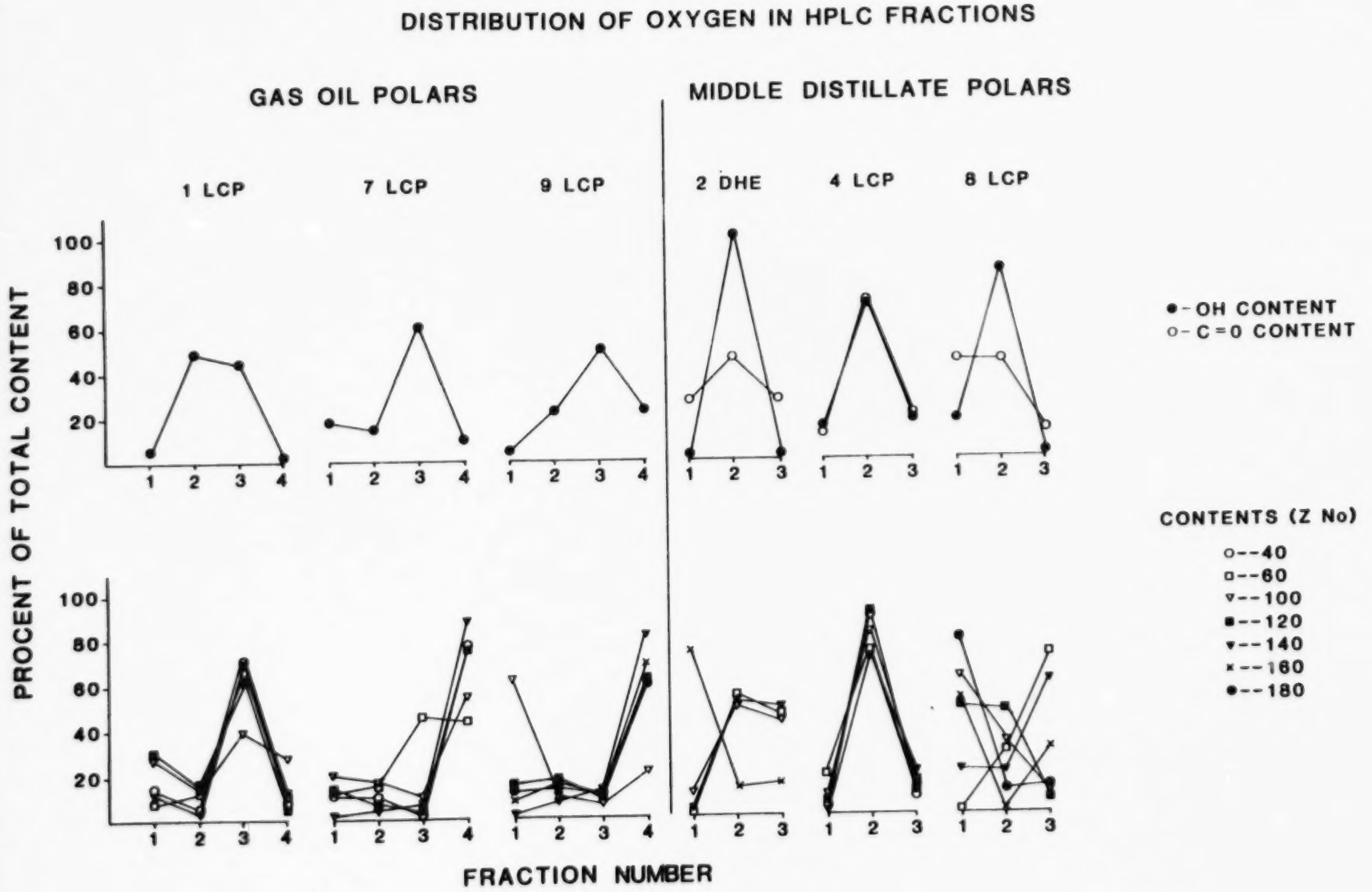

DISTRIBUTION OF OXYGEN IN HPLC FRACTIONS
GAS OIL POLARS
MIDDLE DISTILLATE POLARS
1 LCP
7 LCP
9 LCP
2 DHE
4 LCP
8 LCP
PROCENT OF TOTAL CONTENT
FRACTION NUMBER
●-OH CONTENT
o-C=O CONTENT
CONTENTS (Z No)
o--40
□--60
▽--100
■--120
▼--140
×--160
●--180

Fig. 10

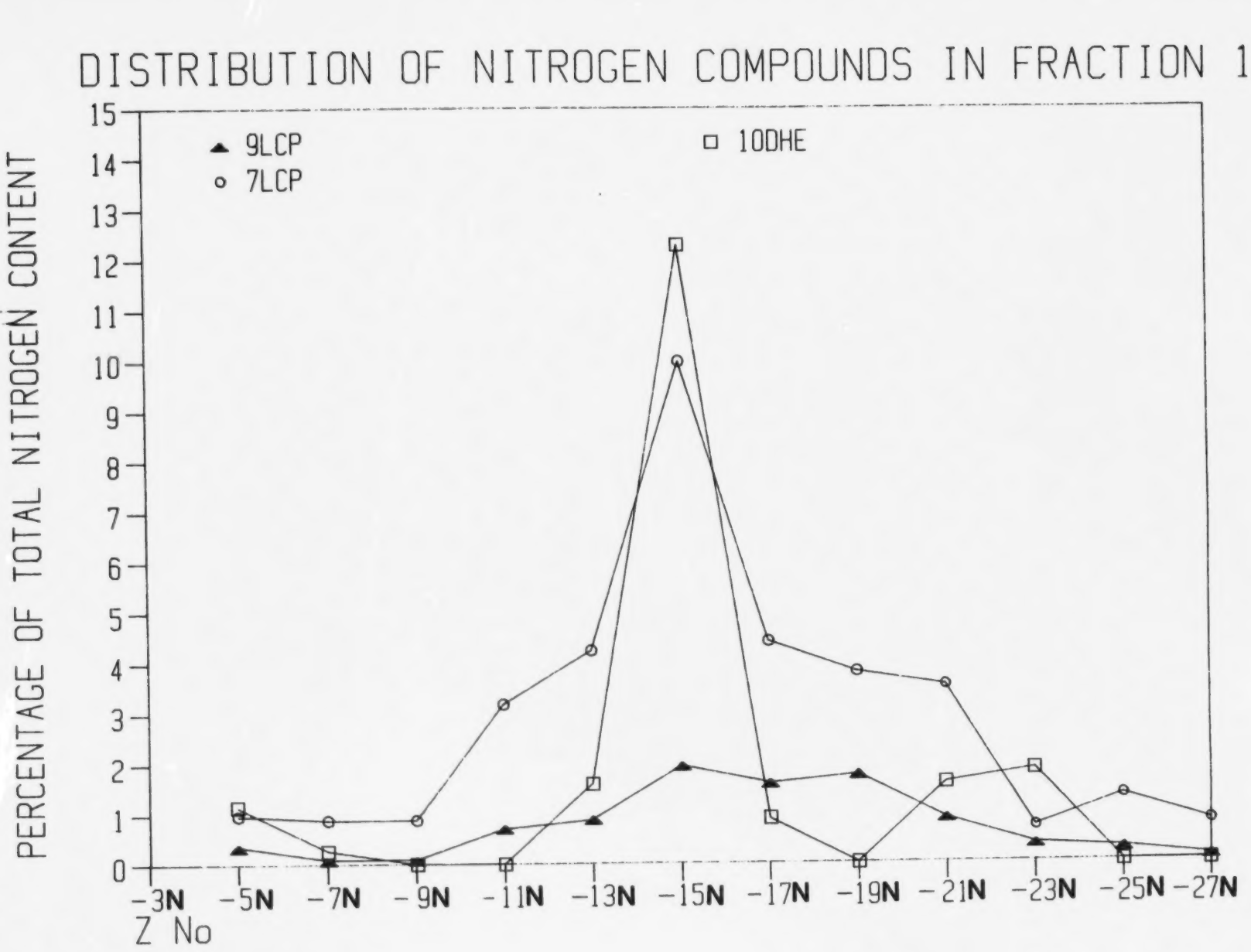

DISTRIBUTION OF NITROGEN COMPOUNDS IN FRACTION 1
PERCENTAGE OF TOTAL NITROGEN CONTENT
9LCP
7LCP
10DHE
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-3N
-5N
-7N
-9N
-11N
-13N
-15N
-17N
-19N
-21N
-23N
-25N
-27N
Z No

Fig. 11A

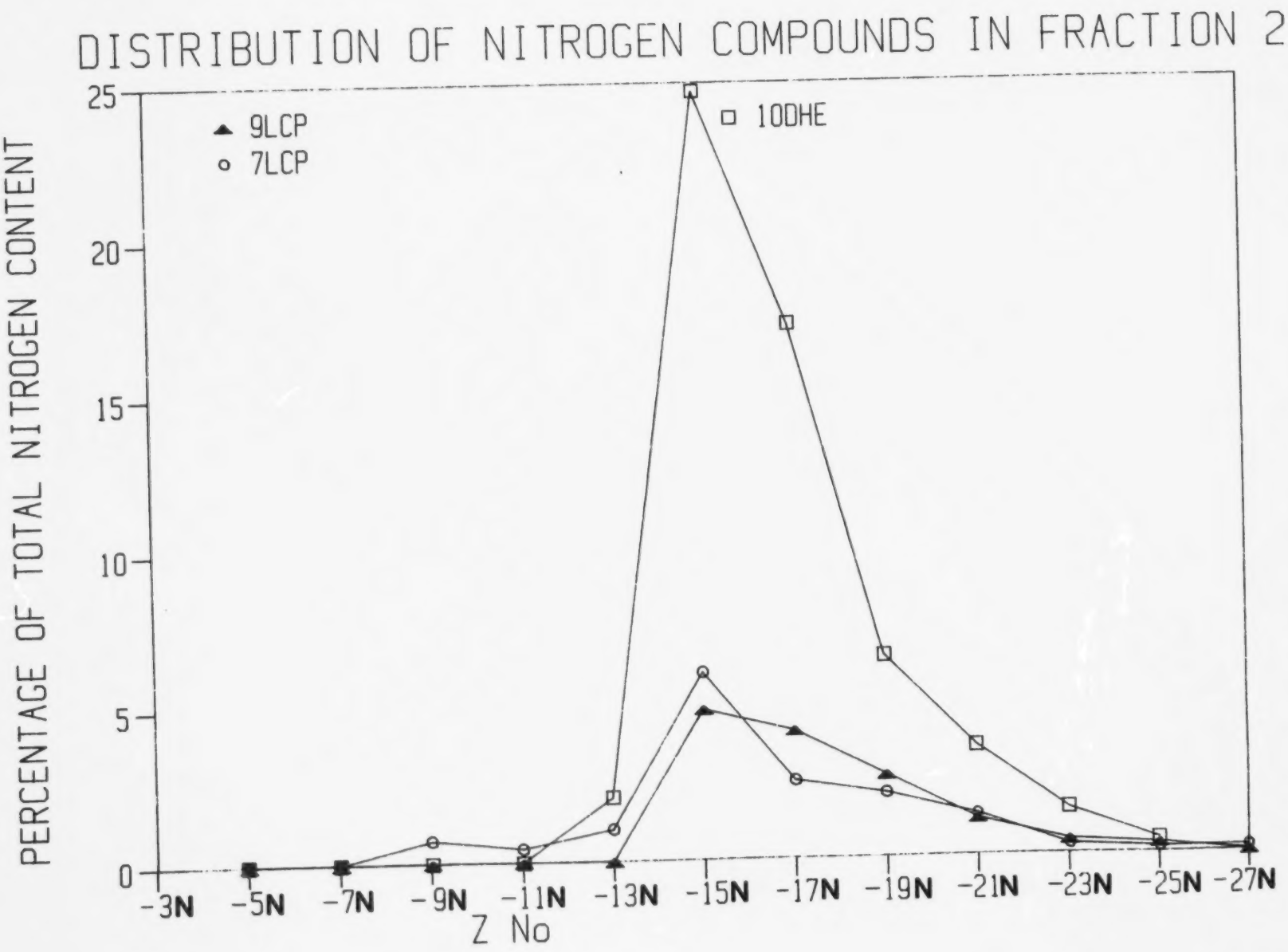

DISTRIBUTION OF NITROGEN COMPOUNDS IN FRACTION 2
PERCENTAGE OF TOTAL NITROGEN CONTENT
25
20
15
10
5
0
9LCP
7LCP
10DHE
-3N
-5N
-7N
-9N
-11N
-13N
-15N
-17N
-19N
-21N
-23N
-25N
-27N
Z No

Fig. 11B

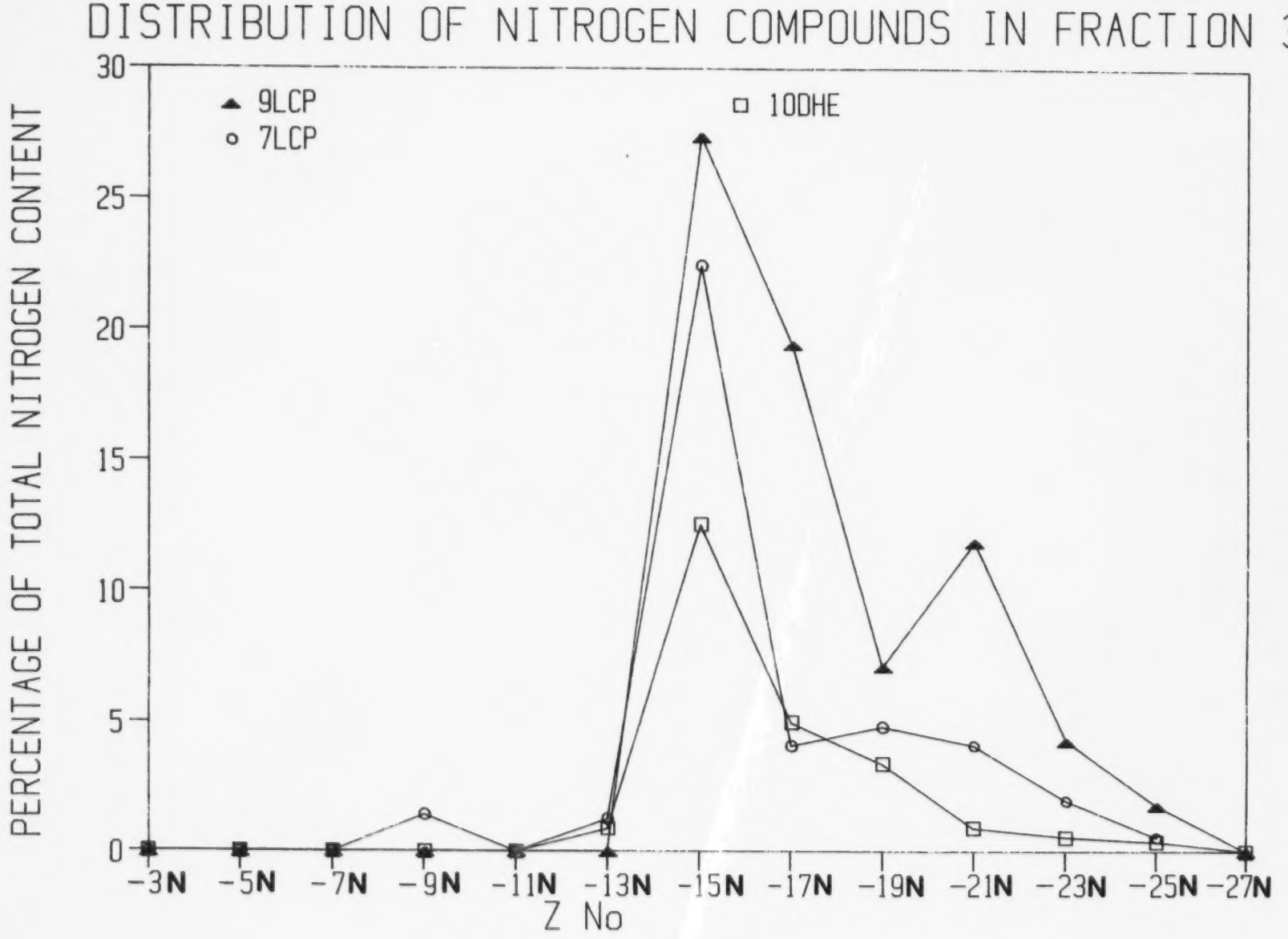

DISTRIBUTION OF NITROGEN COMPOUNDS IN FRACTION 3
PERCENTAGE OF TOTAL NITROGEN CONTENT
9LCP
7LCP
10DHE
30
25
20
15
10
5
0
-3N
-5N
-7N
-9N
-11N
-13N
-15N
-17N
-19N
-21N
-23N
-25N
-27N
Z No

Fig. 11C

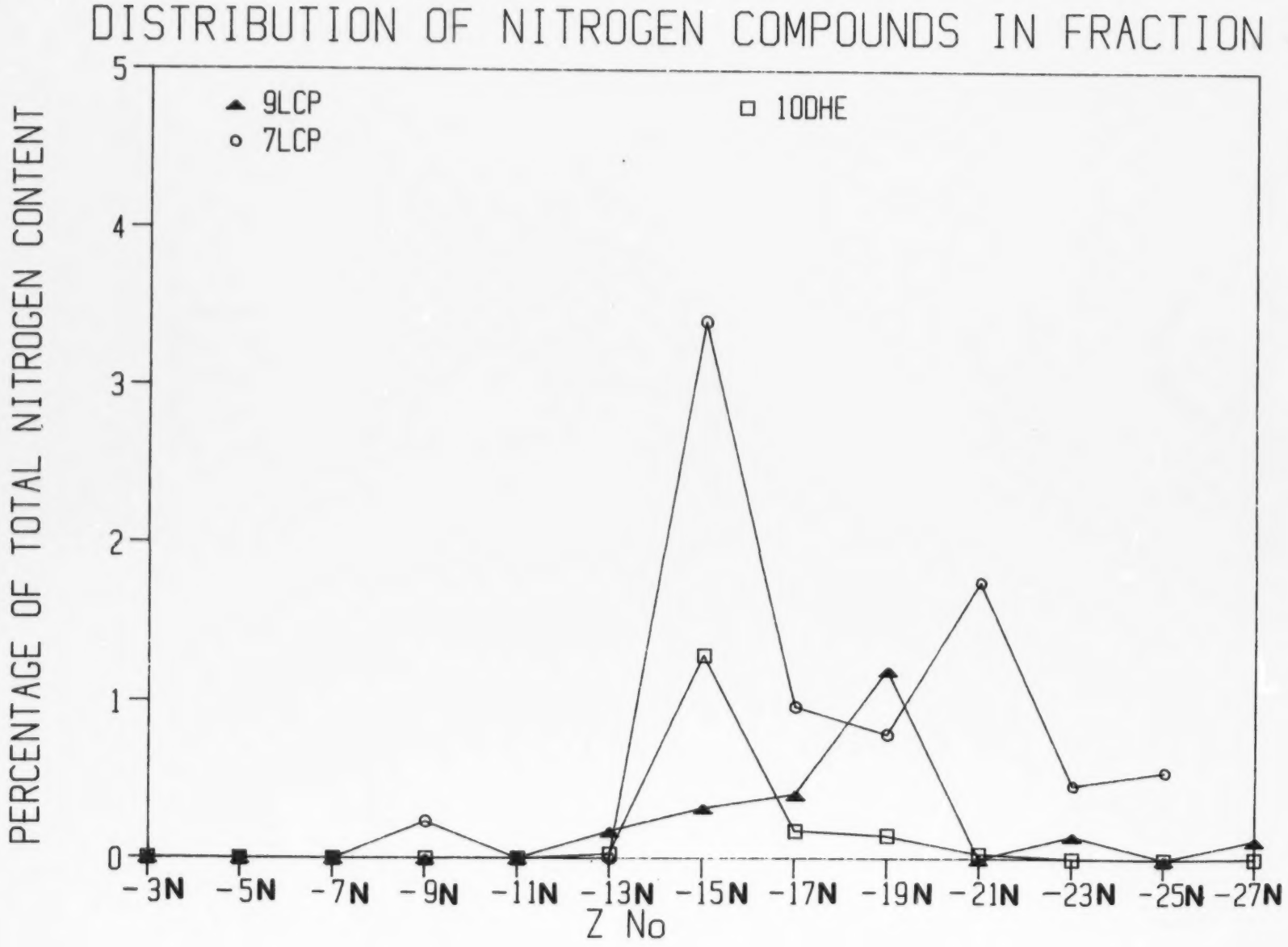

DISTRIBUTION OF NITROGEN COMPOUNDS IN FRACTION 4
PERCENTAGE OF TOTAL NITROGEN CONTENT
9LCP
7LCP
10DHE
5
4
3
2
1
0
-3N
-5N
-7N
-9N
-11N
-13N
-15N
-17N
-19N
-21N
-23N
-25N
-27N
Z No

Fig. 11D

TABLE 2

Samples

Fraction	Abbreviations Assigned to Samples
Athabasca Bitumen Overhead (gas oil)	1*, 1 DHR**, 1 LCR*** 1 DHE**, 1 LCP***
Athabasca Bitumen Overhead (middle distillate)	2, 2 DHR, 2 LCR 2 DHE, 2 LCP
Syncrude Coker Effluent (naphtha)	3, 3 DHR, 3 LCR 3 DHE, 3 LCP
Syncrude Coker Effluent (middle Distillate)	4, 4 DHR, 4 LCR 4 DHE, 4 LCP
Syncrude Coker Effluent (gas oil)	5, 5 DHR, 5 LCR 5 DHE, 5 LCP
Athabasca Bitumen DRB Effluent (naphtha)	6, 6 DHR, 6 LCR 6 DHE, 6 LCP
Athabasca Bitumen DRB Effluent (gas oil)	7, 7 DHR, 7 LCR 7 DHE, 7 LCP
Syncrude Synthetic Crude Oil (middle Distillate)	8, 8 DHR, 8 LCR 8 DHE, 8 LCP
Syncrude Synthetic Crude Oil (gas oil)	9, 9 DHR, 9 LCR 9 DHE, 9 LCP
Mildly Hydrotreated Syncrude Synthetic Gas Oil	10, 10 DHR, 10 DHE

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* single digit - untreated (raw) distillate
** DHR and DHE - DMSO/H_2O raffinate and DMSO/H_2O extract, respectively
*** LCR and LCP - LC raffinate and LC polar fractions, respectively

TABLE 3A YIELDS, SULFUR AND NITROGEN CONTENTS

	Syncrude Raw Coker Crude Oil								Syncrude Synthetic Crude Oil							
	Yield %	S %	N ppm	N_{basic} ppm	Fractionation, wt.% 1	2	3	Recov.	Yield %	S %	N ppm	N_{basic} ppm	Fractionation, wt.% 1	2	3	Recov.
Naphtha																
Untreated sample		1.79	123	128												
LC polars	1.7		2523		5.4	20.1	26.2	51.7								
LC raffinate		1.96	38	22												
DMSO extract*	3.9	5.35	385	364.3												
DMSO raffinate*			81	61.7												
Middle Distillate																
Untreated sample		4.23	1076	901						0.1	167	50				
LC polars	3.6		15 499		10.2	49.2	14.3	73.9	0.8		11 964		33.5	53.5	11.0	98.0
LC raffinate			180								49					
DMSO extract	5.6	7.27	6425	1905	54.5	26.2	8.1	88.5	1.25	0.83	6789	2017	60.5	15.5	24.0	100.0
DMSO raffinate		4.00	629	560.4						0.04	84	75.6				
Nitroethane extract									38.7	0.09	994	128.9				
Gas Oil																
Untreated sample		5.24	2836	1316						0.4	1510	230				
LC polars	14.1		13 818		33.5	43.0	9.8	86.3	4.8		18 528		35.5	48.0	12.1	95.6
LC raffinate			403								187					
DMSO extract	6.1	6.62	10 357	3530	45.9	35.6	13.0	94.5	3.5	0.53	9690	2017	57.2	32.3	7.3	96.8
DMSO raffinate		4.94	2010	1009						0.43	852	230				
Nitroethane extract	44.3	5.66	5522	1009					18.8	4.00	4330	1121				
Nitroethane raff.			2814								787					

* Obtained as follows: extraction with DMSO/H_2O (94:6) followed by polar phase shaken with equal amount H_2O, then NaCl added to salt out extractees to be re-extracted with hexane.

TABLE 3B YIELDS, SULFUR AND NITROGEN CONTENTS Cont'd

	Athabasca Bitumen DRB Effluent								Athabasca Bitumen Overhead							
	Yield %	S %	N ppm	N_{basic} ppm	Fractionation, wt.% 1	2	3	Recov.	Yield %	S %	N ppm	N_{basic} ppm	Fractionation, wt.% 1	2	3	Recov.
Naphtha																
Untreated sample		1.06	127	117.7												
LC polars	0.2		11 548		22.8	19.7	23.2	65.7								
LC raffinate		1.34	15.7	4.2												
DMSO extract*	3.1	5.87	632	560.4												
DMSO raffinate*			28	18.7												
Middle Distillate																
Untreated sample										3.08	368	319.4				
LC polars									1.9		10 436		10.9	40.8	13.0	64.7
LC raffinate										2.79	44	8.4				
DMSO extract									10.8		4028		30.7	30.2	21.4	82.3
DMSO raffinate										3.49	238	202				
Nitroethane extract									42.4	3.95	1424	1233				
Nitroethane raff.										2.35						
Gas Oil																
Untreated sample		3.39	2489	1569						4.15	1521	633.2				
LC polars	8.2		18 947		32.8	47.9	15.3	96.0	9.5		10 480		36.2	38.9	14.5	93.9
LC raffinate			275								263					
DMSO extract	3.6	6.12	8296	3587	35.2	28.4	36.3	100.0	3.1	5.81	8323	2690	38.1	37.0	11.7	86.8
DMSO raffinate		3.19	2046	1009						3.69	1287	616				

TABLE 4

Total Oxygen Content of Samples Studied and Their Raffinates

Sample	Oxygen Content W/W%	Sample	Oxygen Content W/W %
1	0.35 ± 0.02	6	0.06 ± 0.01
1 DHR	0.35 ± 0.02	6 DHR	0.15 "
1 LCR	0.14 ± 0.01	6 LCR	0.04 "
2	0.21 ± 0.01	7	0.27 "
2 DHR	0.15 ± 0.01	7 DHR	0.23 "
2 LCR	0.09 + 0.01	7 LCR	0.26 "
3	0.40 ± 0.02	8	0.13 "
3 DHR	0.30 ± 0.02	8 DHR	0.05 "
3 LCR	0.16 ± 0.01	8 LCR	0.20 "
4	0.40 ± 0.02	9	0.11 "
4 DHR	0.17 ± 0.01	9 DHR	0.11 "
4 LCR	0.12 ± 0.01	9 LCR	0.14 "
5	0.42 ± 0.02		
5 DHR	0.40 ± 0.02		
5 LCR	0.27 ± 0.01		

The uncertainty represents the 95 percent confidence level.

TABLE 5 PRELIMINARY INSPECTIONS OF POLAR CONCENTRATES BY GC/MS

DRB Naphtha, LC Polars
- Sample contains primarily Me-, DiMe- and unsubst. Phenol
- Other O-compounds as well as S- and N-compounds are present at low levels

Syncrude Coker Naphtha, DMSO Extract
- Mono Aromatics predominate
- Sample contains fair amount of Thiophenes and Benzothiophenes
- No major N-compounds were detected

Syncrude Naphtha, DMSO Extract
- Only Saturates and Mono Aromatics were detected

Athabasca Bitumen/DRB Naphtha, DMSO Extract
- Sample contains primarily Mono Aromatic and some Oxygen compounds at low concentrations
- High elem. Sulphur is likely due to solvent contamination as there are no S-compounds observed by GCMS

Syncrude 199-385°C Middle Distillates, Nitroethane Extraction
- Extraction appears to be ineffective/sample is mostly Hydrocarbons
- Low concentrations of Carbazoles, Benzothiophenes and Dibenzothiophenes are observed

Athabasca Bitumen Overhead 195-360°C, Nitroethane Extraction
- Extraction appears to be ineffective/sample is mostly Hydrocarbons
- Substantial amounts of Benzothiophenes and Dibenzothiophenes are observed
- Nitrogen compounds are likely present but predominant aromatics cause too much interference

Syncrude Middle Distillate, DMSO Extract
- Di and Triaromatics premominate
- GC/MS observes significant concentrations of Carbazoles (Z-15N) Benzocarbazoles (Z-21N) and Dibenzothiophenes (Z-16S)

TABLE 5 cont'd — PRELIMINARY INSPECTIONS OF POLAR CONCENTRATES BY GC/MS

Syncrude Coker Middle Distillate, DMSO Extract

- Sample contains significant amounts of N-compounds (Indoles -9N, Carbazoles -15N, Acridines -17N, and -19N ... -23N) Sulfur compounds (Dibenzothiophenes -16S and -18S, -10S)

Syncrude Raw Coker Middle Distillate, LC Polars

- Sample poorly resolved by GC/MS - GC limitations
- Contains particularly high concentration of Carbazoles

Athabasca Bitumen Overhead 195-360°C, LC Polars

- Sample poorly resolved by GC/MS - GC limitations
- Contains particularly high concentration of Carbazoles

Note: The LC-polars of Middle Distillates may not completely elute from the GC column (280°C!). They are very high boilers in respect to the distillate that they were extracted from.

Syncrude Raw Coker Naphtha, LC Polars

(el. N ≅2523 ppm @ MW ≅140 → 2.5% N Compounds)

The sample contains substantial amounts (≅25%) of phenols plus other unidentified oxygen compounds in the higher boiling range. N-compounds (pyridines, indoles, quinolines) are present at low concentrations, but they are masked by the predominant aromatic hydrocarbons.

Syncrude Middle Distillate, LC Polars

The sample contains primarily carbazoles and related N-compounds the C_nH_{2n-17N}.....$-21N$ species (≅80%?). Aromatics and aromatic S-compounds make up the remainder of the sample.

TABLE 6 ULTRAVIOLET CHARACTERIZATION OF EXTRACTS AND ABSORBANCES MEASURED FOR DETERMINING CONTENTS OF MONO-, DI- AND POLY-AROMATIC HYDROCARBONS

Origin	Conc. g/L	Cell (cm)	Absorbances of Most Intense Bands	Absorbances at** 198 nm	228 nm	260 nm
Coker Naphtha	0.2172	0.1	213 nm → 0.962 Abs. below 190 nm i.e. olefinic	1.390	0.504	0.218
Coker M.D.	0.0682	0.1	251 nm → 0.486 228 nm → 0.778	0.624	0.778	0.344
Coker Gas Oil	0.0488	0.1	254 nm → 0.442 223 nm → 0.452	0.414	0.440	0.400
Coker Gas Oil*	0.075	0.1	255 nm → 0.414 230 nm → 0.488 195 nm 0.518	(195 nm) 0.518	(230 nm) 0.488	0.390
Syn. Synth. Naphtha	0.312	0.1		(204 nm) 2.048	0.017	0.067
Syn. Synth. M.D.	0.0368	0.1	249 nm → 0.309 209 nm → 0.450	0.382	(227 nm) 0.476	0.199
Syn. Synth. M.D.*	0.0964	0.1	250 nm → 0.091 218 nm → 0.42 (sh) 193 nm 1.094	0.882	(228 nm) 0.30	0.074
Syn. Synth. Gas Oil	0.121	0.1	250 nm → 1.118 238 nm → 1.198 213 nm 1.044	0.992	1.070	0.978
Syn. Synth Gas Oil*	0.134	0.1	255 nm → 0.778 232 nm → 0.934 212 nm 0.998 193 nm 1.170	1.12	0.94	0.732
A.B. DRB Gas Oil	0.0728	0.1	249 nm → 0.662 238 nm → 0.652 225 nm 0.798 207 nm (sh) 0.68	0.626	(225 nm) 0.798	0.514
A.B. M.D.	0.0486	0.1	250 nm → 0.076 225 nm → 0.261 195 nm 0.340	(195 nm) 0.340	(225 nm) 0.261	0.061
A.B. Gas Oil	0.524	0.1	256 nm → 0.439 232 nm → 0.477 213 nm 0.418 192 nm 0.046	0.435	(232 nm) 0.477	0.383

* Extracts obtained employing nitroethane. Other extracts obtained with DMSO/H_2O (94:6)

** These values may be used for determining the absorptivities, provided that average molecular weights of sample are available.

TABLE 7

Gas Chromatographic Analysis of DMSO Extracts
and Corresponding Raffinates using a Thermionic Specific Detector

(Results in ppm Nitrogen w/v)

Boiling Point Range (°C)	Sample Identification									
	3DHE	4DHE	8DHE	6DHE	3DHR	4DHR	8DHR	6DHR	4LCR	4LCP
IBP-115	-	-	-	-	-	-	-	-	-	-
115-254	289	27	8	621	78	-	-	28	107	294
254-355	91	1695	122	10	3	485	-	-	73	2880
355+	5	4703	6659	1	-	144	84	-	-	12588
Total Nitrogen (from Table 3B)	385	6425	6789	632	81	629	84	28	180	15499

TABLE 8A

Naphtha Derived Polars. Distribution of NH and OH groups in HPLC cuts.

	3DHE	3LCP				6DHE	6LCP		
Content		P	1	2	3		P	1	2	3
NH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	not detected		
OH	0.89	10.4	0.0	4.0	2.7	0.35	9.9			

TABLE 8B

Middle Distillate Derived Polars. Distribution of NH and OH groups in HPLC cuts.

	SAMPLE IDENTIFICATION															
	2DHE				2LCP				4DHE				4LCP			
Content	E*	1	2	3	P**	1	2	3	E	1	2	3	P	1	2	3
NH	1.57	0.0	2.12	0.0	2.11	0.23	1.93	I***	4.11	0.25	7.25	I	2.22	0.25	4.06	4.59
OH	3.28	0.18	2.90	6.1	7.88	0.86	3.17	I	5.56			I	8.24	0.54	5.39	4.30

	8DHE				8LCP			
Content	E	1	2	3	P	1	2	3
NH	6.94	0.11	2.72		7.98	0.27	7.80	0.40
OH	0.31	0.09	1.17		4.1	0.38	1.27	0.0

*E - extract
**p - LC polars
***I - insoluble

TABLE 8C

Gas Oil Derived Polars. Distribution of NH and OH groups in HPLC cuts.

	SAMPLE IDENTIFICATION															
	1DHE				1LCP				5DHE				5LCP			
Content	E*	1	2	3	P**	1	2	3	E	1	2	3	P	1	2	3
NH	7.96	0.72	12.3	8.9	4.26	2.48	3.29	0.0	I 8.96	0.58	14.6	11.0	4.1	0.02	6.95	0.0
OH	2.23	0.0	2.3	9.0	2.21	1.21	1.51	0.0	I 2.24	0.0	2.71	0.0	2.0	0.6	13.2	1.1

	9DHE				9LCP				7DHE				7LCP			
Content	E	1	2	3	P	1	2	3	E	1	2	3	P	1	2	3
NH	14.4	1.30	31.1	18.4	15.2	3.87	25.3	10.6	6.97	0.40	7.92	0.0	9.38	0.99	9.58	2.81
OH	0.3	0.47	0.0	0.0	0.0	0.0	0.0	0.0	3.23	0.0	2.23	7.41	5.13	0.91	5.10	0.0

*E - extract
**P - LC polars
***I - insoluble

TABLE 9

HPLC Fractionation into Four Fractions

Sample	HPLC Fractionation			IR Characterization	
	Recovery wt %	Subfraction	Distribution, wt %	NH Content, % w/w carbazole	OH Content, % w/w hydroxy standard
1 LCP	86.0	1	30.2	0.4	0.2
		2	11.9	11.6	5.0
		3	38.0	3.5	1.4
		4	5.9	3.1	0.5
7 DHE	96.0	1	33.1	0.3	1.0
		2	9.4	16.2	3.0
		3	18.9	18.5	6.0
		4	34.6	1.1	1.4
7 LCP	96.0	1	32.0	1.2	0.4
		2	14.0	14.6	4.8
		3	31.0	11.5	5.1
		4	19.0	6.3	3.8
9 LCP	77.5	1	23.5	3.8	ND*
		2	20.0	41.1	ND
		3	33.6	32.6	ND
		4	18.9	7.2	ND

* ND - not detected

TABLE 10

Characteristics of Catalytically Denitrogenated Syncrude Gas Oil (SGO)

Full Range Sample (10)	Total Nitrogen content, ppm	438
	Gas Oil 360°C+, % w/w	59.5
360°C+ Fraction (10 DHE)	Total Nitrogen content, ppm	619
	Basic Nitrogen content, ppm	158.3
	Total Sulfur content, % w/w	0.12
	$DMSO/H_2O$ (96:4) extraction	
	- yield, % w/w	2.09
	- extract nitrogen content, ppm	12 331
	- NH content, % carbazole w/w	13.6
	- OH content, % standard w/w	0.2
	- raffinate nitrogen content, ppm	341
	HPLC fractionation of extract	
	- sample recovery, % w/w	89.5
	- sample distribution, % w/w	41.6, 25.8, 17.4, 4.7
	- NH content, % carbazole w/w	3.44, 33.9, 34.7, 1.41
	- OH content, % standard w/w	2.4, 1.2, 1.4, 0.4

TABLE 11

Middle Distillates - C=O Determination

Sample Origin	Sample	C=O Content % w/w	Comments	HPLC Fractions: Fraction	C=O Content % w/w	Comments
Athabasca Bitumen	Extract 2 DHE	5.5	Mostly acid	1	11.0	Broad C=O near 1720, acid or esters and some keto
				2	19.1	Sharp 1735 - mostly acid
				3	16.7	Mostly acid
Overhead	Polars 2 LCP	24.1	Mostly acid	1	32.2	Equal acid/ester and keto
				2	33.8	Essentially all acid
				3	23.3	Mostly acid
Syncrude Coker	Extract 4 DHE	4.1	Almost equal intensity peaks at 1730 acid 1705 keto 1665 ?	1	5.9	Equal acid and keto
				2	5.5	Mostly keto
				3	22.6	Mostly keto
Effluent	Polars 4 LCP	19.7	About equal intensity peaks at 1730 acid 1700 keto	1	11.2	Similar intensity acid & keto
				2	10.5	Similar intensity acid & keto
				3	9.7	Similar intensity acid & keto
Syncrude Synthetic Crude	Extract 8 DHE	6.6	Mostly keto type	1	9.5	Mostly keto
				2	19.4	approx. equal acid & keto
				3	46.9	Essentially all acid
	Polars 8 LCP	28.8	Mostly keto (1710)	1	64.1	Mostly keto
				2	39.5	Mostly keto
				3	59.7	Acid & keto bands

TABLE 12

GC/MS Characteristics of Collected HPLC Cuts
Resolved Extracts and LC Polars Derived from Napthas and Middle Distillates

Sample	HPLC Cut	Characteristics/Comments
2DHE	1	Predominant compounds types Z-18,-16,-16 S,-2 O/-1 0,-14/-16 O
	2	As above and carbazoles - approx. 25%
	3	20% of injected sample eluted
2LCP	1	Predominantly Z-18,-16,-16 S
	2	Predominantly Z-15 N approx. 25%, -17 N,-9 N,-16 O
	3	Strongly retained, Z-15 N present
	3a	Silylation of 3 proves effective (TMS ions)
3LCP	1	Primarily Z-6 S and some Z-6 O (phenols)
	2	Z-6 O approx. 25%, Z-6 S approx. 50%, Z-11 N approx. 7%
	3	as 2; Z-6 O approx. 35%, Z-6 S approx 65%
4DHE	1	Order of predominance: Z-16 S,-18,-22,-10 S,-16,-14,-12
	2	Z-15 N approx. 60%, -17 N approx. 10%, -19 N approx 5%, 21 N approx. 5%, -18 and -15 S approx 5%
	3	Z-15 N approx 50%, -21 N approx. 25%, some -16 S and -23 N
4LCP	1	Order of predominance: Z-16,-18,-14,-10,-16 S,-12,-10 S
	2	Z-15 N approx. 65%, -17 N approx. 15%, -19 N approx 5%, -21 N approx 10%, -16 S approx. 5%
	3	Z-15 N approx. 65%, -17 N approx. 10%, -21 N approx. 20%, -19 N approx. 3%, some -9 N and -11 N
6LCP	1	Increase in MW observed comparing to sample of origin
	2	As above
	3	Strongly retained
	3a	Unsuccessful silylation of 3
8DHE	1	Estimated predominance Z-16,-18.,-16 S,-14,-10 S,-12
	2	Z-15 N approx 80%, -17 N approx. 8%, -19 N approx. 4%, -21 N approx 7%
	3	No useful GC/MS data
8LCP	1	Mostly aromatic hydrocarbons
	2	Z-15 N (80-90%), some -17 N... 21 N
	3	No useful GC/MS data
	3a	Unsuccessful silylation of 3

TABLE 13

Total Nitrogen Content of HPLC Fractions, ppm

Sample	Sample Nitrogen Content	HPLC Separation into 4 Fractions			
		Fraction	Yield, %	N Content	Solvent*
1LCP	10480	1	30.2	8592	Toluene
		2	11.9	6613	Toluene
		3	38.0	5297	Toluene
		4	5.9	1267	THF
7DHE	8296	1	33.1	1711(1102)	THF (Toluene)
		2	9.4	7172(4588)	THF (Toluene)
		3	18.9	3997(3778)	THF (Toluene)
		4	34.6	411	THF
7LCP	18947	1	32.0	9792	Toluene
		2	14.0	10000	Toluene
		3	31.0	11800	THF
		4	19.0	3750(3733)	THF (Toluene)
9LCP	11964	1	23.5	2053	Toluene
		2	20.0	3556	Toluene
		3	33.6	11235	THF
		4	18.9	1347	THF
10DHE	12331	1	41.6	3815	Toluene
		2	25.8	18000	Toluene
		3	17.4	11370(10250)	THF(Toluene)
		4	4.7	3114	THF

*Solvent used for dissolving HPLC fraction. Concentrations ranged from 10-50 mg/mL.

TABLE 14

Mass Balances for HPLC Separation

Determination	Mean value of recovery factor, $\bar{X}$	Standard Deviation, S	Method
Weight	94	4	Weighing
NH content	68	19	IR Spectroscopy
OH content	62	27	"
C=O content	163	95	"
Molecules containing single N atom*	90	21	HRMS

* Based on Σ(mass %)z
where z = -5N, -9N, -11N,
-15N, -17N, -23N,
-27N, -29N

TABLE 15

Positive Identifications of Predominant Components

Sample	Fraction	HRMS	GC/MS	Identification
3 LCP	2	High contents of Z -4 O, -6 O and -10 O	Primarily contains Z -6S and -6 O	Benzylmercaptans, phenols
	3	High contents of Z -4 O and -6 O	"	"
2 DHE	2	Predominant Compound types Z -15N		Carbazoles
2 LCP	2	Predominant compound types Z -15N		Carbazoles
4 DHE	2	"		"
	3	"		"
4 LCP	2	"		"
	3	Predominant compound types Z -15N, -21N		Carbazoles and benzocarbazoles
8 DHE	2	High contents Z -15N, -17N	Mostly Z -15N, -17N, -21N	Carbazoles
8 LCP	2	Predominant compound types Z -15N		Carbazoles